TITLE OF INVENTION

A Catalyst System for Controlled Polymerization

INVENTORS

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CROSS REFERENCE TO RELATED APPLICATIONS

This application is a nonprovisional application claiming priority from U.S.

Application Serial No. 60/238,812 filed on October 6, 2000.

FIELD OF INVENTION

10   The present invention relates to catalysts for atom transfer radical

polymerization processes.   Specifically, the present invention relates to a hybrid

catalyst system comprising transition metal complexes held in close conjunction with a

solid support and of a soluble ligand, or soluble transition metal complex or desorbed

catalyst.

15   BACKGROUND OF THE INVENTION

There is a continuing effort in polymer chemistry to develop new

polymerization processes and new polymers.   A relatively recent development in

polymer chemistry has been the development of controlled or living polymerization

processes. A controlled or living polymerization process is one in which chain transfer

and termination reaction are essentially nonexistent relative to the polymer propagation

reaction. These developments have led to the production of polymers that exhibit

macro functionality and to the development of functional polymers that possess specific

5 chemical reactivity. The new polymers extend the level of control available to materials

engineers in processing polymers and using polymers as building blocks in, or

components for, subsequent material forming reactions, such as copolymerizations,

chain extensions and crosslinking reactions, and interaction with substrates, including

dispersed solids.

10 A significant economic hurdle which continually needs to be overcome in

this effort is to provide the benefits of controlled polymerization from available low cost

monomers in available commercial process equipment. These long term objectives

have provided the backdrop, or driving force, for the continuing advances in controlled

polymerization of radically (co)polymerizable monomers, disclosed in earlier patent

15 applications, and provide the incentive to extend, simplify and make more robust the

process known as atom transfer radical polymerization (ATRP).

The recently developed ATRP process and polymers developed from the

classic ATRP reaction are described in U.S. patent applications Serial No. 09/018,554

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and 09/534,827, the entire contents of which are hereby incorporated herein by reference. Methods for exercising control over many parameters in a catalytic process for the controlled polymerization of a wide range of free radically (co)polymerizable monomers have been described in publications authored or co-authored by Krzysztof

5 Matyjaszewski and others. *See* for example, Wang, J.S. and Matyjaszewsk, K., *J. Am. Chem. Soc.*, vol. 117, p.5614 (1995); Wang, J.S. and Matyjaszewsk, K., *Macromolecules*, vol. 28, p. 7901 (1995); K. Matyjaszewski et al., *Science*, vol. 272, p.866 (1996); K. Matyjaszewski et al., "Zerovalent Metals in Controlled/"living" Radical Polymerization," *Macromolecules*, vol. 30, pp. 7348-7350 (1997); J. Xia and K.

10 Matyjaszewski, "Controlled/ "Living" Radical Polymerization. Homogenous Reverse Atom Transfer Radical Polymerization Using AIBN as the Initiator," *Macromolecules*, vol. 30, pp. 7692-7696 (1997); U.S. Patent Application 09/126,768, the entire contents of which are hereby incorporated by reference; U.S. Patents Nos. 5,807,937, 5,789,487, 5,910,549, 5,763,548, 5,789,489, 5,945,491, 6,111,022, 6,121,371, 6,124,411 and U.S.

15 Patent Applications 09/034,187, 09/018,554, 09/431,871, 09/359,359, 09/359,591, 09/369,157, and 09/534,827 the entire contents of each are hereby incorporated herein by reference. The subtle interactions between the parameters have been further explored and implementation of the teachings disclosed in these publications has

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allowed the preparation of many inherently useful novel materials displaying control

over functionality and topology, and production of novel tele-functional building blocks

for further material forming reactions, resulting from application of the site specific

functional and topological control attainable through this robust controlled

5   polymerization process for free radically (co)polymerizable monomers.

The system or process employed to gain control over the polymerization

of free radically (co)polymerizable monomers has been described in earlier applications

as comprising the use of four components: (i) an initiator molecule; (ii) a transition metal

compound having (iii) an added or associated counterion and the transition metal

10   compound complexed with (iv) a ligand(s).   The initiator molecule, or polymerization

originator molecule may be any molecule comprising one or more radically transferable

atom(s) or group(s) capable of participating in a reversible redox reaction with the

transition metal compound.   The transition metal compound may include an added or

associated counterion and comprise a transition metal salt.   So that all reactive

15   oxidation states are soluble to some extent in the reaction medium, the transition metal

may be complexed with the ligand(s).   The components of the system may be

optimized to provide more precise control for the (co)polymerization of the free radically

polymerizable monomers.   *See* U.S. Patent No. 5,763,548, the entire contents of which

are hereby incorporated herein by reference.

In an embodiment known as "reverse" ATRP, the initiator molecule described above can be formed in-situ by reaction of a free radical with the redox conjugate of the transition metal compound. Other components of the polymerization

5   system such as the choice of the radically transferable atom or group, counterion initially present on the transition metal, and optional solvent may influence the process. U.S. Patent No. 5,807,937 provides as an example of a single molecule containing a combination of functions, a complex in which the counterion and ligand components are in one molecule. The role of a deactivator, the "persistent radical," or for ATRP, the

10   transition metal redox conjugate, is also described in U.S. Patent No. 5,807,937.

While not to be limited to the following description, the theory behind ATRP disclosed in the previous work is that polymerization proceeds essentially by cleavage (and preferably essentially homolytic cleavage) of the radically transferable atom or group from the initiator molecule or, during the polymerization process the

15   dormant polymer chain end, by a reversible redox reaction with a complexed transition metal catalyst, without any strong carbon-transition ($C-M_t$) bond formation between the active growing polymer chain end and the transition metal complex. Within this theory as the transition metal complex, in a lower active oxidation state, or in its activator state,

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activates the initiator or dormant polymer chain end by homolytically removing the

radically transferable atom or group from the initiating molecule, or growing polymer

chain end, in a reversible redox reaction, an active species is formed that allows other

chemistry, essentially free radical based chemistry to be conducted.   The transition

5   metal complex in the higher oxidation state, the redox conjugate state or deactivator

state, transfers a radically transferable atom or group to the active initiator molecule or

growing chain end, thereby reforming the lower oxidation state transition metal complex.

When free radical based chemistry occurs, a new molecule comprising a radically

transferable atom or group is also formed.   In prior publications, the catalytically active

10   transition metal compound, which can be formed *in situ* or added as a preformed

complex, has been described as containing a range of counterions.   The counterion(s)

may be the same as the radically transferable atom or group present on the initiator, for

example a halide such as chlorine or bromine, or may be different radically transferable

atoms or groups.   An example of the latter counterion is a chloride counterion on the

15   transition metal compound when the initiator first contains a bromine.   Such a

combination allows for efficient initiation of the polymerization followed by a controlled

rate of polymerization, and has additionally been shown to be useful in certain

crossover reactions, from one set of (co)monomers to a second set of (co)monomers,

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allowing efficient formation of block copolymers.

ATRP is one of the most promising methods in the field of controlled/"living" radical polymerizations, one which can be applied to a wide variety of monomers and provide well defined polymers. However, one of the commercial

5   limitations of ATRP is the presence of a transition metal complex, which is often present in concentrations above what is normally considered catalytic levels that can be left in the products.   Therefore is some applications, the catalyst should be removed after the polymerization.   Several processes for the preparation and use of immobilized ATRP catalysts have been proposed to reduce the concentration of catalyst remaining in the

10   polymer product.   Processes have been attempted using ATRP catalysts immobilized on silica, crosslinked polystyrene beads or attached to polymer chain; all of which can provide an efficient way conducting the polymerization or be used for separating and recycling of the catalyst.   However, generally these techniques still suffer, to some degree, from a lack of the control over the polymerization originating from the

15   heterogeneous nature of the process.   Not wishing to be limited by the description of the mechanism, this loss of control may be attributable to an insufficient deactivation rate of the growing radical which results from the slow diffusion of the active growing polymer chains to the immobilized deactivator complexes, which leads to a much higher

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molecular weight and broader molecular weight distribution than in homogeneous

systems.

Thus, there exists a need for an catalyst system for controlled

polymerization that is easily separable from the reaction medium and provides sufficient

5   control over the process.   More, specifically there exists a need for a catalyst system

for ATRP which allows sufficient deactivation of the growing polymer chains to provide a

controlled polymerization process.

SUMMARY OF THE INVENTION

The present invention meets these needs by providing a polymerization

10   process comprising polymerizing radically (co)polymerizable monomers in the presence

of a system comprising an initiator comprising one or more radically transferable

atom(s) or group(s) and a catalyst system comprising a transition metal, one or more

counterions, a ligand attached to a solid support, and a soluble ligand.   The present

invention also provides polymerization process comprising polymerizing radically

15   (co)polymerizable monomers in the presence of a system comprising an initiator

comprising one or more radically transferable atom(s) or group(s), an attached transition

metal complex, and a soluble transition metal complex.

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The ligand or the transition metal complex may be physico- or physicochemically or chemically bound to the surface of a solid support through ionic bonding, physisorption, chemisorption, Van der Waals forces, coordinate or covalent bonding. The soluble transition metal complex or ligand may be formed by changing a

5   (co)polymerization condition to cause at least a portion of the transition metal complex or ligand to be unbound from the surface of the added solid. A process for the removal and recycle of a supported transition metal catalyst complex from a polymerization reaction medium comprising separating the supported transition metal catalyst from the reaction medium, and contacting the supported transition metal catalyst with a reducing

10   agent is also provided.

DESCRIPTION OF FIGURES

Figure 1 is a graph illustrating the dependence of $\ln([M]_0/[M])$ versus time for various controlled and uncontrolled polymerization processes;

Figure 1a is a graph illustrating the dependence of molecular weight versus conversion

15   for and ideal controlled polymerization and the effects of the slow initiation, chain transfer and coupling of uncontrolled polymerization processes on the molecular weight change versus conversion;

Figure 2 is a table illustrating examples of the polymers which may be produced by

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controlled polymerization processes;

Figure 3 is a graph illustrating the calculation of the maximum concentration of residual copper in the polymer;

Figure 4 is graph of the increase of number average molecular weight versus

5   conversion for the polymerization of methyl methacrylate with bpy-CuBr supported catalyst on polystyrene beads (8 μm) using a 3% of soluble Me6TREN-CuBr to supported bpy;

Figure 5 is a graph of the GPC curves from polymerization of MMA with bpy-CuBr supported on Polystyrene bead (8 μm) using a 1% soluble $Me_6TREN-CuBr_2$ to

10   supported bpy.

DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention overcomes the diffusion limitation by providing a new catalyst concept comprising the use of a small amount of soluble deactivator in addition to the immobilized catalyst system was examined.   This

15   disclosure therefore is directed towards extending the utility of transition metal mediated controlled radical (co)polymerization processes by defining conditions for the controlled polymerization of radically (co)polymerizable monomers using a hybrid catalyst system.

The hybrid catalyst of the present invention comprising a transition metal

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complex attached to a solid support, providing catalyst immobilization, and a low level of

soluble catalyst which may be formed by, for example, providing a soluble ligand or

alternatively a low level of unattached transition metal complex present in the

polymerization medium, or other means to allow the catalyst deactivator to be more

5   readily available to the growing polymer chain. The hybrid catalyst system may initially

comprise the combination of an attached catalyst system and an unattached ligand, or

an attached transition metal and an unattached transition metal complex, or an attached

catalyst system acting in conjunction with other components or parameters of the

process that can form an active complex for deactivation of the growing polymer chain

10   under the conditions of the polymerization. In such a hybrid system the transition metal

complex is attached by being physico- or physicochemically or chemically bound to the

surface of a solid support through ionic bonding, physisorption, chemisorption, Van der

Waals forces, coordinate or covalent bonding.

In one such a hybrid catalyst system the transition metal complex is held in

15   close conjunction with the solid support by chemical bonding through utilization of an

attached ligand but is made available to the "living" controlled polymerization occurring

in close contact with the solid support through interaction with an added soluble ligand,

without the invention being limited by the explanation, we believe that this hybrid system

operates through a transitory formation of a low level of transition metal complex in the

liquid phase next to the solid support.   In an alternate system the hybrid catalyst

system can be formed through interaction of a preformed transition metal catalyst

complex with a solid support by being physico- or physicochemically or chemically

5   bound to the surface of a solid support through ionic bonding, physisorption,

chemisorption, Van der Waals forces, or coordinate bonding and act as a hybrid catalyst

system through the presence of an excess of a soluble ligand of different non-bonding

or non-absorbing structure, again without being limited by the explanation we believe

that this allows a transitory formation a low level of transition metal complex in the liquid

10   phase next to the solid support.   By judicious selection of the soluble ligand one can

provide for the "soluble" transition metal complex to be predominately the redox

conjugate of the attached transition metal complex and therefore preferentially selected

for deactivation of the growing radical.   As a further method of forming a hybrid catalyst

system there is an attached transition metal catalyst complex and a lower level of

15   unattached transition metal complex, preferentially comprising the deactivator oxidation

state of the catalyst complex, interacting to control the polymerization process.

In a further option for the formation of a hybrid catalyst system, the ligand can be

chosen so that it desorbs from the solid support to a sufficient degree to directly form a

hybrid system under polymerization conditions and then reforms a solid supported

catalyst system under conditions used for catalyst removal and catalyst recycle. A

non-limiting choice for forming such a hybrid catalyst system under this option is to add

to the reaction medium a low boiling solvent that desorbs the necessary concentration

5   of catalyst from the support, preferentially in the redox conjugate state. After the

polymerization, the solvent can be removed under the influence of heat or vacuum,

extraction or other separation technique known in the art, thereby driving the catalyst to

return to the solid support for substantially complete separation from the product. For

copper based catalysts, for example, this process may include a polar solvent.

10   Another method of forming such a desorbable hybrid catalyst system is to design a

transition metal complex that is strongly adsorbed to the solid surface at one

temperature but is sufficiently desorbed at the polymerization conditions to control the

polymerization.

The term hybrid can be considered, without limiting us to the specific definition,

15   as an essentially biphasic polymerization system, one in which the bulk of the transition

metal complex is closely held in contact with an added solid, so that low levels of the

transition metal would be found in the contacting polymerization medium at the end of

the polymerization process, but the transition metal is made sufficiently present, and

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active as a catalyst in the polymerization system, by interaction with a soluble ligand

added to the polymerization medium, or with an added soluble transition metal complex,

or made available through selection of the reaction conditions, or by addition of other

components of the reaction medium to provide a controlled polymerization process.

5   For the present purposes "polymers" include homopolymers and

(co)polymers (unless the specific context indicates otherwise), which may be block,

random, statistical periodic, gradient star, graft, comb, (hyper)branched or dendritic

polymers.   The "(co)" parenthetical prefix in conventional terminology is an alternative,

viz., "(co)polymer means a copolymer or polymer, including homopolymer, while

10   "(co)polymerizable means a monomer that is directly polymerized by the polymerization

mechanism being discussed and additionally includes a comonomer which can only be

incorporated into the polymer by copolymerization.   Similarly "(hyper)" is meant to

incorporate the concept that the degree of branching along the polymer backbone can

vary from a low degree of branching up to a very high degree of branching.

15   Here, and elsewhere in the text the word "control and/or controlled" means

that in the polymerization process conditions are defined whereby the contributions of

the chain breaking processes are insignificant compared to chain propagation, so that

polymers with predetermined molecular weights, low polydispersity and high

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functionalities are achievable.

It is widely accepted that controlled polymerization should display the
following features.

Feature 1. First-order kinetics behavior, i.e. the polymerization rate (R_p)

5   with respect to the monomer concentration ([M]) is a linear function of time. This is due

to the lack of termination, so that the concentration of the active propagating species

([P*]) is constant.

$$R_p = \frac{-d[M]}{dt} = k_p[P^*][M] \qquad\qquad (1.1)$$

10    $$\ln\frac{[M]_0}{[M]} = k_p[P^*]t = k_p^{app}[P^*]t \quad \text{(if [P*] is constant)} \qquad (1.2)$$

k_p is the propagation constant.   The result of eq.1.2 is illustrated in Figure 1.

This semilogarithmic plot is very sensitive to the change of the

concentration of the active propagating species. A constant [P*] is revealed by a straight

15   line, and an upward curvature indicates an increased [P*], which occurs in case of a

slow initiation. On the other hand, a downward curvature suggests the decrease of [P*],

which may result from termination or some other side reactions such as the catalytic

system being poisoned.

It should also be noted that the semilogarithmic plot is not sensitive to

chain transfer process or slow exchange between different active species, since they do

not affect the number of the active propagating species.

Feature 2.   Predetermined degree of polymerization (X_n), i.e. the number

5   average molecular weight (M_n) is a linear function of monomer conversion.

$$X_n = \frac{M_n}{M_0} = \frac{\Delta[M]}{[I]_0} = \frac{[M]_0}{[I]_0}(conversion) \qquad\qquad (\textbf{1.3})$$

This result comes from a constant number of chains throughout the

10   polymerization, which requires the following two conditions:

a)   the initiation should be sufficiently fast so that nearly all chains start to grow

simultaneously; and

b)   no chain transfer occurs to increase the total number of chains. Figure 1a

illustrates the ideal growth of molecular weights with conversion, as well as the

15   effects of slow initiation and chain transfer on the molecular weight evolution.

Importantly, the evolution of molecular weights is not very sensitive to

chain termination, since the number of chains remains unchanged. Only when coupling

reaction plays a significant role for polymers with very high molecular weights, is the

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effect of termination observable on the plot.

Feature 3. Narrow molecular weight distribution. Although this feature is very desirable, it is not necessarily the result from a controlled polymerization, which requires only the absence of chain transfer and termination, but ignores the rate of

5 initiation, exchange and depropagation. Substantial studies [Gold, 1958 #84; Coleman, 1963 #88; Matyjaszewski, 1995 #85; Hsieh, 1996 #81; Matyjaszewski, 1996 #86] indicate that in order to obtain a polymer with a narrow molecular weight distribution, each of the following five requirements should be fulfilled.

i. *The rate of initiation is competitive with the rate of propagation.* This condition

10 allows the simultaneous growth of all the polymer chain.

ii. *The exchange between species of different reactivities is faster than propagation.* This condition ensures that all the active chain termini are equally susceptible to reaction with monomer for a uniform growth.

iii. *There must be negligible chain transfer or termination.*

15 iv. *The rate of depropagation is substantially lower than propagation.* This guarantees that the polymerization is irreversible.

v. *The system is homogenous and mixing is sufficiently fast.* Therefore all active centers are introduced at the onset of the polymerization.

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An essentially narrow molecular weight distribution is attained which should yield

a Poison distribution, as quantified in eq.1.4.

$$\frac{X_w}{X_n} = \frac{M_w}{M_n} = 1 + \frac{X_n}{(X_n + 1)^2} \cong 1 + \frac{1}{X_n} \qquad \textbf{(1.4)}$$

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According to eq.1.4, polydispersity (M_w/M_n) decreases with increasing

molecular weight. A polymerization that satisfies all five prerequisites listed above is

expected to have a final polymer with a polydispersity less than 1.1 for X_n greater than

10.

10   *Feature 4.*   Long-lived polymer chains.   This is a consequence of the

negligible chain transfer and termination. Hence, all the chains retain their active

centers after the full consumption of the monomer. Propagation resumes upon the

introduction of additional monomer. This unique feature enables the preparation of block

copolymers by sequential monomer addition.

15   The significance of controlled polymerization as a synthetic tool is widely

recognized. Polymers having uniform and predictable chain length are readily available.

Controlled polymerization provides the best opportunity to control the bulk properties by

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selection and control of various aspects of the multitude of variations in composition, functionality and topology at a molecular level. The result of such control the preparation of polymeric materials is shown schematically in Figure 2.

This control over polymer structure or composition is not, or should not be

5   lost as one moves towards conducting the polymerization with the disclosed hybrid catalyst, a catalyst comprising an "attached" transition metal complex and "available" transition metal complex. The "available" transition metal complex can be formed *in-situ* by the sole addition of a "free" ligand which forms a transitory soluble active transition metal complex by interacting with the attached transition metal, the first hybrid

10   mediated polymerization process taught in this application, or can be added as a second soluble transition metal complex, optionally in the redox conjugate state; or a further component of the polymerization process can be added to desorb sufficient transition metal complex from the solid support to allow formation of a hybrid system, or the reaction conditions can be changed sufficiently from conditions during the

15   polymerization to allow resorption of the desorbed catalyst from the reaction medium. Preferably, as little as 5% of ligand or transition metal complex may be soluble to provide control over the polymerization.

In one case in point the transition metal complex is "attached", or held in

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close contact with a resin, by using one or more ligands directly attached to the solid

support in the formation of the transition metal complex. The transition metal is made

fully accessible to the polymerization mixture by the presence of a soluble ligand in the

polymerization medium. One illustration of the improved process using an organic

5   support, described in detail below, is the use of DOW ion exchange resins with attached

amine functionality, which acts as a ligand for a transition metal compound to form a

supported transition metal complex catalyst. In another example, an amine based

ligand is attached to an inorganic support such as silica through design of a ligand that

interacts with the surface of the silica. The supported transition metal complex

10   comprising such an attached ligand, forms a hybrid catalyst complex after the addition

of a soluble ligand, such as tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN), to the

polymerization medium and the hybrid system supports a controlled polymerization

process. Me$_6$TREN is known to form a complex with copper that has a very high

deactivation rate constant.

15   Without being limited by the explanation we envision that the use of a

ligand such as Me$_6$TREN is a particularly useful choice since Me$_6$TREN preferentially

forms a soluble complex with the redox conjugate of the transition metal, i.e. the higher

oxidation state of the transition metal, forming a complex that is active in the

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deactivation of the growing radical chain, which is essential if one desires a

polymerization process that exhibits high initiator efficiencies and provides polymers

exhibiting narrow molecular weight distribution, in contrast to prior art supported catalyst

disclosures. This is one of the most preferred approaches to the formation of a hybrid

5   catalyst system since in a commercial operation the feed to the solid supported

transition metal complex can just additionally comprise a low concentration of liquid,

soluble ligand in the monomer/initiator solution being fed to the bed of supported

catalyst. In a further option, one can add a low concentration of a reducing agent to

reduce the concentration of the attached redox conjugate which would tend to increase

10   due to unavoidable termination reactions. The reducing agent can comprise any

species that reacts with a transition metal in its higher oxidation state and reduces it to a

lower oxidation state and can include sources of free radicals or a transition metal in a

zero oxidation state.

In a non-limiting description of the mechanism for controlled

15   polymerization using such a hybrid catalyst system an attached transition metal forms

an active group from an initiator or growing polymer chain by transfer of a radically

transferable group from the molecule to the transition metal complex thereby forming

both the redox conjugate of the transition metal complex and an active molecule that

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can add monomers. This active polymer chain end can be preferentially deactivated or returned to a dormant polymer chain end comprising a radically transferable atom or group by transfer of such a radically transferable atom or group from a soluble redox conjugate of the transition metal complex wherein the ligands of the transition metal

5   complex are soluble in the polymerization medium. This forms a soluble transition metal complex in which the transition metal is in a lower oxidation state, but if the ligand chosen to form the soluble transition metal has been chosen to preferentially exist as the higher oxidation state complex then this newly formed lower oxidation state soluble transition metal complex, will remove a radically transferable atom or group from an

10 attached higher transition metal complex reforming the preferred hybrid catalyst system comprising an attached complex of lower oxidation state and soluble complex of higher oxidation state in addition to having allowed a controlled increase in the molecular weight of the polymer in contact with the hybrid catalyst system.

An alternate embodiment is to directly add the low level of a preformed

15 soluble transition metal complex to the solid supported transition metal complex thereby directly forming the desired hybrid catalyst system in the absence of an added excess of soluble ligand. In a further embodiment additional control over the polymerization is obtained if the low level of soluble transition metal complex added to form the hybrid

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catalyst system is the redox conjugate of the attached transition metal complex. In

such a system a small amount of the deactivator can exist in the solution phase to

afford fast deactivation of the growing radical and reduce the diffusion barrier presented

by requiring diffusion of the growing radical chain end to a supported deactivator. To

5   obtain a successful hybrid catalyst system, the deactivator should meet several

requirements. The deactivation rate constant for the soluble deactivator should be high

and the soluble deactivator should be more reducing than the immobilized catalyst to

thereby be reconverted to the higher oxidation state species continuously and rapidly

after the deactivation step.

10   A further process that can be used to form a hybrid catalyst system is to

add a preformed transition metal complex, formed by complexation of a transition metal

compound with a ligand that has been pre-selected to strongly interact with an added

solid. The complex is added to the selected solid support and thereafter held in close

conjunction with such an added solid solely through ionic bonding, physicosorption,

15   chemisorption, Van der Waals forces, or coordinate bonding and be converted into, or

act as, a hybrid system through the presence of a low level of excess media soluble

ligand of different non-bonding or non-absorbing structure which, again without being

limited by the explanation, we believe can form a transitory low level of active transition

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metal complex in the liquid polymerization phase comprising the monomers next to the

solid support; or in conjunction with a low concentration of added soluble transition

metal complexes. Again, as an alternative approach to an operating hybrid transition

metal complex system one can add the redox conjugate of the transition metal, formed

5   with a media soluble ligand, to the polymerization process. In this system in which the

transition metal complex is added to a solid support and is held through ionic bonding,

physicosorption, chemisorption, Van der Waals forces, or coordinate bonding the ligand

can be selected to allow sufficient transition metal complex to desorb from the added

solid under polymerization conditions to function to control the polymerization. In such

10   a system with one selected ligand the system acts as a hybrid catalyst through selection

of the conditions for polymerization to additionally form the hybrid catalyst. In such a

system the added solid support can comprise any solid support that does not interact

with the polymerization to additionally form the hybrid catalyst. In such a system the

added solid support can comprise any solid support that does not interact with the

15   polymerization but allows sufficient transition metal complex to desorb and act to control

the polymerization. Such solids include silica, aluminates and clays.

CN$_6$TREN was chosen as a first exemplary ligand for such a hybrid

catalyst system based on such adsorption/desorption of the transition metal complex

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through hydrogen bonding of the ligand to the inherent functionality present on the

surface of the added solid.   This ligand would be strongly adsorbed onto a polar

substrate such as a silica particle. In the initial experiments we determined that in a

homogeneous system this ligand did provide a transition metal complex that provided a

5   controlled polymerization. In the presence of silica however the molecular weight

distribution of the polymer produced with such a strongly adsorbed hybrid catalyst

system was close to 2.0.   This indicates that the complex was very strongly absorbed

onto the silica surface and as with the ligand supported catalyst the redox conjugate of

the transition metal catalyst was not readily accessible to the growing active polymer

10   chain.   This would indicate that one should to tailor the strength of the physisorption to

the surface to obtain optimum control over the polymerization.   This can be

accomplished by adding a solvent to assist in the desorption at the polymerization

temperature.   Another procedure would be to modify the substituents on the ligand to

control the strength of the absorption/desorption and another would be to tether specific

15   functionality to the surface and then fully control the interaction of the ligand with the

attached functionality.   The concentration of the tethered functionality on the surface of

the particle can be also be controlled as can the strength of the interaction between the

tethered functionality and the functionality on the ligand. The type of functionality used

to tether the ligand to the surface can comprise a substituant on the ligand including

hydroxy, amine, imine, as well as other functionality.

A further preferred embodiment of such a hybrid catalyst system, one that

can be utilized to regenerate the catalyst during recycle in a batch polymerization

5   system, or during extended operation of a continuous polymerization system while

employing a solid supported catalyst, is the optional embodiment of utilizing the added

soluble ligand to regenerate the catalyst by transportation of a transition metal in the

zero oxidation state to the solid supported transition metal complex to thereby reduce

the excess redox conjugate transition metal complex formed by the unavoidable low

10   level of termination reactions, even in such a well controlled polymerization process.

This is demonstrated in the experimental section in a non-limiting example

applicable to a batch polymerization system utilizing copper as the attached transition

metal where after the solid catalyst complex is separated from the formed polymer the

free ligand can be added to the monomer solution and copper zero can be added to the

15   mixture as a solid, wire, mesh or powder in sufficient concentration, and for sufficient

time, to reduce any additionally formed redox conjugate.   One method is to immerse a

copper rod into the mixture for a short, though sufficient time to form a complex with the

added free ligand and thereby be transported to the attached redox conjugate.   When

the transition metal complex has been adjusted to form the desired mixture of transition

metal oxidation states then initiator is added to initiate the controlled polymerization.

In a continuous operation the free ligand can used to transport a sufficient,

low concentration of transition metal in the zero oxidation state to compensate for any

5   build up in concentration of the redox conjugate.   The amount of required transition

metal complex in the zero oxidation state can be calculated or monitored by

examination of the conversion level at constant flow.   If the conversion level decreases

then increased metal zero complex, or other reducing agent such as a source of free

radicals, is required to increase the initiation or activation activity of the supported

10   transition metal catalyst.   If the molecular weight distribution of the formed polymer

increases then lower levels of metal zero complex, or added reducing agent, is required

since reduced levels of available redox conjugate leads to poorer control over the

deactivation process.

While this application was in transition from a provisional application to an

15   application a patent application WO 00/75198 was published.   This application

describes "A method for preparing a supported catalyst system and its use in a

polymerization system" and was filed June 3, 1999.   While it claims to utilize a "hybrid

catalyst system" it is not the hybrid catalyst system if this invention.   WO 00/75198

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describes a dual catalyst system for the polymerization of olefins and describes a catalyst system that should provide for the preparation of two different polymers. The system is of course still transfer dominated but the principle must be different from the instant invention disclosed herein wherein we must really have a single catalyst system,

5   one that involves a kind of shuttle, with the individual components of the catalyst constantly changing but providing a single homogeneous polymer as the product of the polymerization process.

There has been a continuing effort to make the controlled radical

10   polymerization process known as ATRP as environmentally benign and as low cost a process for the preparation of functional materials as possible.   One concern expressed about the processes disclosed in disclosed in U.S. Patents 5,763,546; 5,807,937; 5,789,487; 5,945,491; 6,111,022; 6,121,371; 6,124,411 and U.S. Patent Applications 09/034,187; 09/018,554; 09/431,871; 09/359,359; 09/359,591; 09/369,157;

15   and 09/534,827; processes for the preparation of polymers displaying control over the polymer molecular weight, molecular weight distribution, composition, architecture, functionality and the preparation of molecular composites and tethered polymeric structures is the presence of a transition metal in the immediate product of the reaction.

Although several improvements directed at catalyst separation, catalyst recycle and increased catalyst activity were disclosed in the above patents and patent applications, a need persisted, one we believed has now been overcome, to thwart this potential barrier to commercialization. WO 99/28352 describes an ATRP process utilizing a

5   pyridineimine based supported ligand. The present disclosure overcomes the poor control over molecular weight distribution found in such prior art biphasic catalyst systems by providing systems wherein the redox conjugate of the attached activator transition metal complex, the deactivator is available to the growing polymer chain.

When the biphasic system described in the prior art is employed for

10   controlled radical polymerization an area of particular concern is access of the growing polymer chain to the persistent radical for the polymerization system. In ATRP this means that the active growing polymer chain should have access to the transition metal complex in the higher oxidation state and that such a redox conjugate transition metal complex should comprise a radically transferable atom. Example 269 in application

15   09/534,827 first describes the use of a biphasic supported catalyst, and while the polymerization was successful the molecular weight distribution of the formed polymer was greater than 2.25 throughout the polymerization. In the work described in WO 99/28352 by Haddleton the reported molecular weight distribution (MWD) for the

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polymers formed in the presence of a solid supported catalyst are also quite broad; in a

paper, Haddleton; *et al.* Macromolecules **1999**, *32*, 4771, the MWD is reported to be

around 1.5.   Work of another group in this field, Shen *et al*, also report MWD close to

1.5   Both these prior art observations of poor control over molecular weight distribution

5   can be attributed to poor access to the persistent radical for the controlled

polymerization process, this phenomenon will exacerbated as the molecular weight of

the polymer increases due to viscosity and resulting diffusion effects.

When a supported ligand is used to prepare a transition metal complex, as

described in the prior art, an understanding of the means to produce an effective low

10   level of "homogeneously" available, or appropriately partitioned, transition metal redox

conjugate was not available within the chemistry of the prior art processes.   The

approaches we now disclose make the redox conjugate of the transition metal complex

available in the polymerization medium while retaining low instantaneous metal

concentration in the system.   One such approach is to add low levels of soluble

15   unattached ligand or soluble transition metal complexes to the system forming a hybrid

catalyst system.   The ligand can be selected to act as a shuttle between the

polymerization medium and the supported catalyst.

This approach additionally allows an expedient method for reactivation of

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the formed hybrid catalyst during catalyst recycle for batch polymerization systems or during continuous operation wherein the soluble ligand is used to shuttle transition metal in a zero oxidation state to the supported catalyst regenerating the transition metal complex by reducing the concentration of the formed redox conjugate.

5   This hybrid catalyst concept was first evaluated using a polystyrene based ion exchange resin with an attached amine functionality, one that could function as a ligand in the formation of a transition metal complex suitable as a catalyst for ATRP. The reaction scheme to prepare the immobilized catalyst (CuBr/PS-bpy) is shown in Scheme 1. The 4,4'-dimethyl-2,2'-bipyridine was covalently immobilized on a Merrifield

10   resin initially containing a benzyl chloride functional group to minimize leaching of the catalyst from the support. The Merrifield resin was based on a lightly crosslinked polystyrene (5 mol% divinylbenzene) with the average particle size of 8 µm. The metallation of the ligand with CuBr afforded the immobilized catalyst (1.15 x 10^{-3} mol-ligand/g-catalyst, determined by elemental analysis).

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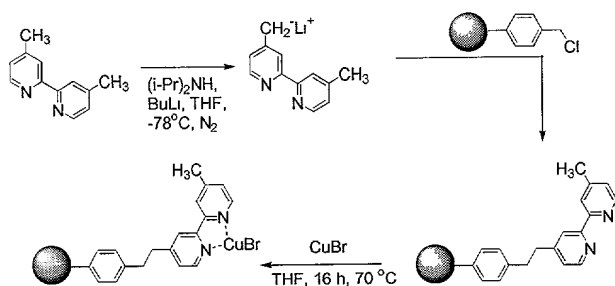
Scheme 1.

The exemplary soluble ligand chosen to demonstrate conversion of this

5   attached catalyst complex into a hybrid complex was based on the Me_6TREN ligand,

although any ligand described as suitable for forming a catalyst active in ATRP would

also find utility. The addition of an excess of soluble ligand alone converted this

adsorbed catalyst into a hybrid system.

Other approaches evaluated to provide a hybrid catalyst system are to

10   utilize a preformed transition metal catalyst complex that is held in close conjunction

with an added solid such as alumina, silica, crosslinked polystyrene beads and/or clay

through being physico- or physicochemically or chemically attached to the surface of the

solid support through ionic bonding, physisorption, chemisorption, Van der Waals forces,

coordinate or covalent bonding, and converted into a hybrid system by the presence of

15   a low level of excess soluble non-bonding ligand, soluble transition metal complex or

desorbable transition metal complex. This approach to a hybrid catalyst is

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demonstrated by the preparation of a diamine ligand for support of an ATRP catalyst on

an inorganic support such as silica.   This was accomplished by the synthesis of N,N,N'-

trimethyl-N'[3-(trimethoxysilylporpoxycarbonyl)ethyl]-ethylenediamine shown below in

scheme 2.

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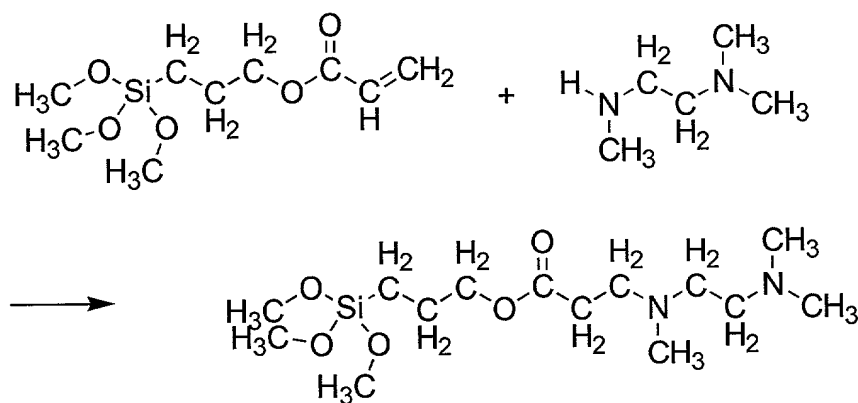
Scheme 2.

This diamine based ligand for the preparation of a transition metal

10   complex suitable for use as an ATRP catalyst has an attached trimethoxy silyl group for

immobilization on silica was synthesized through Micheal addition reaction of amine.

The transition metal can also be attached to a solid support, such as silica,

though hydrogen bonding, in such a case the transition metal is attached by strong

adsorption forces and not a formal chemical bond.   The concept is that the temperature

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of the polymerization sufficient catalyst can desorb from the surface of the particle to

provide a partitioned catalyst and be reabsorbed under conditions used for recovery of

the polymer.   One ligand used to evaluate this concept was CN6TREN which would be

strongly adsorbed onto a solid polar substrate.

5   Another approach to obtaining reverse binding architecture through

supermolecular assembly between the ligand and the matrix using hydrogen bonding,

one that could be particularly useful in the construction and use of such supermolecular

structures as catalysts, is to examine the effect of a spacer between the binding sites

and the bonding sites.   2-Ureidopyrimidin-4-ones was used since strong non-covalent

10   binding can be obtained via multiple hydrogen bond arrays.   With this unit in the ligand,

ultra strong non-covalent coupling can be achieved at low temperature between the

ligand and the support matrix, while free ligand should be available at high temperature.

BPOMA   BPUMA

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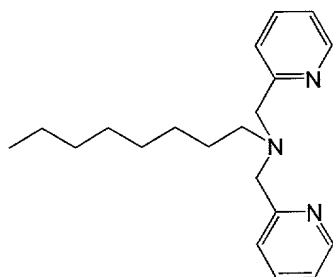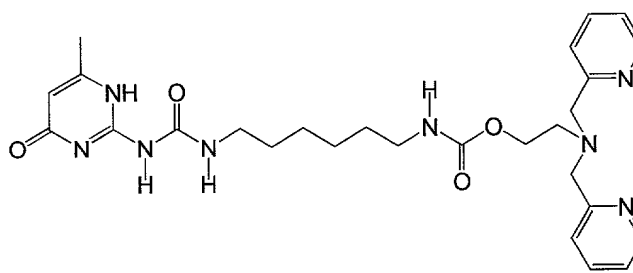
EXPERIMENTAL SECTION: DISCUSSION

The hybrid catalyst system discussed in this application can be used in both continuous biphasic polymerization systems or in batch polymerization systems. The examples described below exemplify a batch polymerization system wherein

5   monomers, optional solvent, and a low concentration of free ligand, or added soluble transition metal complexes wherein the transition metal is present in the desired oxidation state and with the desired counterion if required, is added to a reactor containing the transition metal complex attached to a solid substrate either directly through chemical bonding of the ligand to the solid, or indirectly through a substituant

10   present on the ligand that further interacts with the added solid as defined above. The biphasic reaction mixture is agitated, or stirred, or the liquid phase is pumped around, or a fixed bed of catalyst is employed as the stirrer to mix the liquid intimately with the solid, or any other process that can dynamically bring the monomers and growing polymer chains into dynamic contact with the transition metal complex/solid is employed, such

15   that after an appropriate time, at an appropriate temperature and pressure, the conversion of monomer to polymer has progressed to prepare a polymer of desired molecular weight; then the product is removed from the solid comprising the transition metal complex by filtration or centrifugation under reaction conditions or conditions other

than those employed for the polymerization. The solid is optionally washed with solvent or monomer before reuse. Residual monomer and optional solvent, which can be selected to assist in the formation of the transition metal complex Mechanism

The overall action of the hybrid catalyst system is summarized in Scheme

5 3. Because the rate constant of activation with Cu^I/bpy is in the range of $k_a \sim 10^0$ L mol^{-1} s^{-1}, the activation of polymeric alkyl halide should not be significantly affected by a slow diffusion of the polymeric chains to the solid immobilized catalyst ($k_{diff} \sim 10^5$ L mol^{-1} s^{-1}). The activation process can therefore readily be performed by the immobilized catalyst (CuBr/PS-bpy), present in large excess to the deactivator. However, diffusion of

10 polymer coils to the surface of the solid support can become a rate-determining step in the deactivation process for a completely immobilized catalyst ($k_d \gg k_{diff}$), particularly at high conversion. On the contrary, if a soluble deactivator ($CuBr_2$/Me$_6$TREN) is present in the solution phase this species can deactivate the active radical efficiently without any diffusion limitation. The rate of the deactivation is in the range of $k_d \sim 10^7$ L mol^{-1} s^{-1}.

15 The resulting CuBr/Me$_6$TREN may rapidly reconvert to $CuBr_2$/Me$_6$TREN by abstracting halogen from the immobilized catalyst ($CuBr_2$/PS-bpy) thereby completing the catalytic cycle. Overall, the soluble deactivator may act as a "shuttling" agent that delivers the halogen from the solid immobilized catalyst to growing polymeric radicals to achieve an

effective deactivation process.

$$R_n\text{-Br} \quad \text{CuBr/PS bead-bpy} \quad \text{CuBr}_2/\text{Me}_6\text{TREN} \quad R_{n+m}{}^*$$

$k_{a,s} \sim 10^0 \text{ L mol}^{-1}\text{s}^{-1}$
$k_{d,s} < 10^5 \text{ L mol}^{-1}\text{s}^{-1}$

$K = K_{\text{Me}_6\text{TREN}}/K_{\text{bpy}} \sim 10^4$
$k_{ex} \sim 10^7$

$k_a \sim 10^4 \text{ L mol}^{-1}\text{s}^{-1}$
$k_d \sim 10^7 \text{ L mol}^{-1}\text{s}^{-1}$

$$R_n{}^* \quad \text{CuBr}_2/\text{PS bead-bpy} \quad \text{CuBr/Me}_6\text{TREN} \quad R_{n+m}\text{-Br}$$
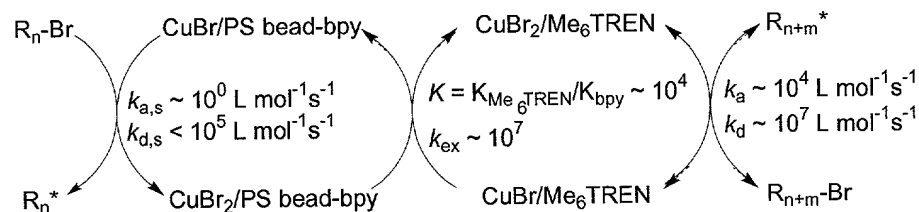
Scheme 3.

Preparation of supported catalyst complex

As further examples of one type of supported hybrid catalyst systems three different kinds of anion exchange resin, supplied by DOW, were used to test their potential first as a material that formed a ligand supported ATRP catalyst and secondly as components of a hybrid catalyst system based on ligand supported transition metal catalysts.   The first two resins are identified as M4195 and XVS 43578, both of which contain bispicolyl amine functionality; XVS 43578 has a more uniform particle size distribution.   The third resin is identified as HPPA and contained an attached hydroxy-picolylamine functionality. The resins were supplied with the amine functionality in the form of sulfate salts.   Therefore it was necessary to neutralize them prior to use to give attached free amine functionality which can play the role of ligand(s) in the formation of

an ATRP catalyst as previously disclosed.   The resins were first washed with freshly

distilled water followed by neutralization with 1M NaOH just to alkaline by PH paper.

During this neutralization procedure the color of the resins change from yellow to brown.

The resins were then washed with fresh water and methanol, successively and dried

5   under vacuum.   The amount of free amine functionality present, and available for use

as a ligand, in the resins was determined by carbon/hydrogen/nitrogen analysis.   The

resin supported ligand-metal complexes were formed by contacting the resin with

$CuBr/CuBr_2$ (8/2 mol/mol).   A measured amount of resin, CuBr, and $CuBr_2$ was

introduced into the reactor in the ratio of [ligand in resin] : [CuBr] : $[CuBr_2]$ = 1 : 0.8 : 0.2

10   followed by evacuation and nitrogen backfilling for 3 times.   Separately, dry

tetrahydrofuran distilled over sodium was degassed by three freeze-pump-thaw cycles.

A measured amount of dry, degassed tetrahydrofuran was introduced into the reaction

flask under nitrogen and the temperature of the reaction bath was increased to 70 ^{0}C

and the reaction, forming the ion exchange resin supported transition metal complex,

15   was allowed to continue overnight.   The obtained transition metal catalyst/resin

complexes were washed twice with dry, degassed tetrahydrofuran and then twice with

pentane. The final resin was dried under vacuum.

General polymerization procedure

Methyl methacrylate polymerization was performed with HPPA and XVS

43578 resins to evaluate them as a supported ATRP catalyst. The polymerizations were

first done *without* any additional soluble ligand such as Me$_6$TREN and the

5   polymerizations showed linear increase of conversion with time but no increase of

molecular weight with conversion. This suggests very poor deactivation of growing

radical, i.e. the resin supported ligand-metal complexes essentially acted solely as

redox initiators and the resulting broad molecular weight distribution can be attributed to

the poor accessibility of growing radical to the Cu(II) centers on the support resins, even

10   though some 20% of the transition metal sites present on the solid were in the form of

the redox conjugate.

One approach to the formation of a hybrid catalyst, using the above

procedure can be an *in-situ* complexation of ligand with the transition metal salt in the

polymerization medium.   HPPA and XVS 43578 resins were neutralized and evaluated

15   using this method.   In these experiments about 3% of Me$_6$TREN-CuBr$_2$ complex

compared to attached or supported ligand was added to the polymerization medium.

This is as an alternative to providing only soluble ligand.   This approach forms an initial

supported catalyst/soluble ligand transition metal complex hybrid system with

immediately accessible redox conjugate.   Such an approach should enhance the

control on polymerization.   Indeed the conversion and molecular weight increased

linearly with time and the MWD was narrow (~1.5), evidence of controlled

polymerization.

5   The polystyrene based resin-bpy-CuBr/Me_6TREN-$CuBr_2$ hybrid catalyst

was tested for methyl methacrylate polymerization with 1 mol% of Me_6TREN-$CuBr_2$ to

attached bpy-CuBr transition metal complex.   The polymerization was found to be fully

controlled.   This is part of a continuing effort to decrease, and ultimately determine a

minimum amount of excess ligand or added transition metal complex, exemplified by

10   Me_6TREN-$CuBr_2$ in the above discussion, necessary to control the reaction.

Minimization of the level of free ligand will decrease the rate at which the catalyst can

migrate through a bed of catalyst in a fixed bed reactor or minimize the amount of

transition metal complexes that will remain in the final product in a batch polymerization

system.   For this reason we propose that the hybrid resin formed to conduct the

15   polymerization contain less than 25% of free unattached, non-complexing ligand,

preferably less than 15%, more preferably less than 10% and most preferably less than

5%.   Such an approach will reduce the overall cost of catalyst in the ATRP system and

simplify the process and minimize transition metal loss from the solid support and

minimize the environmental impact of incorporating an ATRP process into the

processes employed at commercial plant.

The control over polymerization was dramatically improved in an

immobilized catalyst based ATRP by using or forming an additional small amount of

5   reducing soluble catalyst.   High conversion of monomer to polymer is feasible allowing

the formation of polymer with a predetermined molecular weight and a narrow molecular

weight distribution.   The hybrid catalyst system afforded a clear colorless polymer

solution by a simple filtration or sedimentation.   The residual amounts of Cu in the

polymers were greatly reduced less than 1ppm while sufficient control over the

10   polymerization was retained.   The hybrid catalyst system seems to afford a better

method for the successful ATRP with a low concentration of the transition metal in the

polymerization medium.

In summary a hybrid catalyst system can be formed by addition of a low

level of a soluble ligand, or a low level of soluble transition metal complex, to a

15   polymerization system comprising a solid supported transition metal complex.   In such

a system there is a finite concentration of transition metal that could remain in the

formed polymeric product.   We additionally have determined that the molecular weight

distribution of the polymer formed in such a hybrid catalyst system is dependent of the

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concentration of available transition metal complex in the polymerization medium.   As

such it is possible to calculate, the variation of molecular weight distribution and the

maximum calculated value for the residual Cu in polymer produced, based on the added

amount of Me$_6$TREN added. The results of this calculation is shown in Figure 3.   The

5   maximum residual Cu content in polymer can be reduced to 6 ppm while the molecular

weight distribution remains below 1.3.   It is possible that the actual level of copper or

other transition metal will be below this level since there is an additional equilibrium

between the transition metal which complexes with an attached ligand and with the

"free" ligand and this calculation considers only the maximum.

10

EXPERIMENTAL SECTION: EXAMPLES

Preparation of organic supported catalyst

Example 1.   Preparation of PSbead(8 µm)-bpyCuBr catalyst

1a.   Preparation of PSbead(8 µm)-bpy ligand:

15   Feedstock Recipe; PS bead-Cl, 16 g containing 1.104e-2 mol Cl; Dmbpy

10.172 g or 5.521e-2 mol; (IPr)$_2$NH 7.74 mL, 5.521e-2 mol; nBuLi 34.5 mL, 5.521e-2

mol; CuBr 0.3077 g, 2.145e-3 mol (1.2 molar excess).

              After purging the oxygen from a three neck 250 mL round bottom flask by

charging with N_2 follow by vacuum 80 mL of dry THF and 7.8 mL of (iPr)2NH were

added after cooling in a dryice/acetone bath.   34.5 mL of n-BuLi was slowly added to

this mixture and the resulting reaction mixture was further stirred at −78 oC for 2 h. A

solution of dMbpy predissolved in fresh THF was introduced dropwise to the resulting

5   mixture and further stirred at -78 °C for 2 h.. In a separate round bottom flask 16 g

Psbead-Cl was suspended in dry THF under nitrogen purge.   The (IPr)2NH/ nBuLi/

dMbpy solution was transferred to the PSbead suspension by cannula at −78 °C.   The

reaction temperature was allowed to increase to room temperature and the reaction

stirred for an additional 14 h. The product obtained was thoroughly washed with THF

10   and MeOH, two times with each solvent. Drying under vacuum gave the ion exchange

resin with an attached bpy ligand as a yellow powder.

1b.   *Metallation with CuBr.*

The modified ion exchange resin from the above step, PS bead-bpy

(0.9460 g 2.02e-3 mol bpy ligand) was treated with CuBr (0.290 g 2.02e-3 mol).   Both

15   reagents were introduced into 100mL schlenk flask followed by evacuation with high

vacuum and refilled with dehydrated nitrogen for three times and 100 mL of degassed

THF was added to the flask to suspend the reagents and the temperature was

increased to 70 °C. The reaction mixture was stirred at that temperature for 16 h. The

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product was washed thoroughly with 60 mL of degassed THF and hexane, two times each, by decantation. The catalyst was dried under vacuum to provide the supported transition metal complex as a brown powder. The supported catalyst was stored under dry nitrogen.

5   *1c.   Metallation with CuBr/CuBr₂ (8/2)*

Feedstock: PS bead-bpy 0.4963 g (1.062e-3 mol bpy ligand), CuBr 0.122 g (8.50e-4 mol), CuBr2 0.0474 g (2,12e-4 mol). The reactants were introduced into 100mL schlenk flask followed by evacuation with high vacuum and refilling with dehydrated nitrogen for three times. Then 100 mL of degassed THF was added to the flask to

10   suspend the reactants and the temperature was increased to 70 °C. The reaction mixture was stirred at that temperature for 16 h. The product was washed thoroughly with 60 mL of degassed THF and hexane, two times each by decantation. The catalyst was dried under vacuum to obtain brown powder and stored under dry nitrogen.

Example 2.   An alternate preparation of polystyrene bead supported bpy-CuBr

15   *catalyst.*

2a.   Preparation of PSbead(8 μm)-bpy-CuBr catalyst – PS(S)-bpy-102700-1

Recipe: PS bead-bpy 1.79 g; 2.06e-3 mol bpy ligand; CuBr 0.2956 g, 2.06e-3 mol Temperature = 60 °C, reaction time = overnight (~14 h), solvent = THF 70 mL.

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1.79 g of PS bead(8 μm)-bpy and 0.2956 g of CuBr were added to 100mL

Schlenk flask and deoxygenated by evacuation with high vacuum and refilled with

dehydrated nitrogen three times.   70 mL of THF was added to the flask to suspend the

reagents and the temperature was increased to 60 °C.   The reaction mixture was

5   stirred at that temperature for 14 h. The resulting product was washed thoroughly three

times with 60 mL of deoxygenated THF, once with 60 mL of deoxygenated toluene, and

twice with 60 mL of deoxygenated hexane. The dark brown catalyst was dried under

vacuum and stored under dry nitrogen in glove box.

2b.   Preparation of PSbead(8 μm)-bpy-CuBr2 catalyst - PS(S)-bpy-102700-2

10   In order to obtain data for a deactivation rate constant study and material for

evaluation of mixed hybrid catalyst system a PSbead(8 m)-bpy, PSbead(8 m)-bpy-

CuBr2 complex was prepared. The PS bead supported bpy ligand prepared previous

was used for metallation with CuBr2.

Recipe: PS bead-bpy 0.9985 g, containing 1.15e-3 mol bpy ligand; CuBr2

15   0.2565 g 1.15e-3 mol. Temperature = 60 °C, time = overnight (~14 h), solvent = THF 50

mL

0.9985 g of PSbead(8 μm)-bpy and 0.2565 g of CuBr2 were introduced into

100mL Schlenk flask followed by evacuation with high vacuum and refilling with

45

dehydrated nitrogen three times. 50 mL of THF was added to the flask to suspend the solids and the temperature was increased to 60 °C. The reaction mixture was stirred at that temperature for 14 h. The product obtained was washed thoroughly three times with 50 mL of deoxygenated THF, once with 50 mL of deoxygenated toluene and twice with 50 mL of deoxygenated hexane. The dark brown catalyst was dried under vacuum and stored under dry nitrogen in glove box.

Example 3.   *Activation of Commercial resins:*

3a.   *Supported amine ion exchange resins.*

Three different kind of anion exchange resin were obtained from Dow. Resins identified as M4195 and XVS 43578 contain bispicolylamine as an attached ligand, XVS43578 has a more uniform particle size distribution and HPPA contains hydroxypicolylamine functionality. The resins have amine functionality in the form of sulfate salts. Therefore it is necessary to neutralize them prior to use and provide resins with attached free amine which can play a role of ligand in an ATRP catalyst. The resins were first washed with fresh distilled water for 18 h followed by neutralization with 1M NaOH just to alkaline by PH paper (No change of PH for at least two hours should be confirmed). During this neutralization procedure the color of the resins change from yellow to brown. The resins were washed with fresh water and methanol. The obtained

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resins were dried under vacuum for 6h at 60 °C. The amount of free amine ligands available in the resins were determined by C, H, and N analysis (M4195, 2.25e-3 mol Ligand/g cat; XVS43578, 2.20e-3 mol Ligand/g cat; HPPA, 2.21e-3 mol Ligand/g cat)

3b.   Metallation

5   The targeted supported transition metal complexes was to make a ligand-metal complexes with each of the resins with $CuBr/CuBr_2$ (8/2 mol/mol) prior to polymerization experiment. Measured amount of resin, CuBr, $CuBr_2$ ([ligand in resin]:[CuBr]:[$CuBr_2$] = 1:0.8:0.2) were introduced into Schlenk tube followed by evacuation and nitrogen backfilling for 3 times. Separately, dry THF distilled over sodium was degassed by three

10   free-pump-thaw cycles. After measured amount of THF was introduced into the reaction flask under nitrogen, the temperature of the reaction bath was increased to 70 °C and the reaction was allowed to continue for overnight. The obtained resin complexes were washed with dry, degassed THF and pentane for twice each. The final supported transition metal resin was dried under vacuum at 60 °C.

15   *Use of organic media supported catalysts*

Example 4.   ATRP using resin HPPA supported transition metal complexes

(hydroxypicolylamine - CuBr/CuBr2 (8/2 mol/mol))

4a: [Comparison run]

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Composition				
HPPA (metallated)	159 mg		1.44e-4 mol Cu	1.56e-2 mol/L
MMA	4.325 g	4.62 mL	4.32e-2 mol	4.68 mol/L
Toluene		4.62 mL		
2-bromopropionitrile	1.93e-2 g	12.4 μL	1.44e-4 mol	1.56e-2 mol/L

[MMA] : [Initiator] : [HPPA- Cu(I)Br] : [HPPA-Cu(II)Br$_2$] = 300 : 1 : 0.8 : 0.2   Tp = 90 °C.

The reaction components were stirred together in a flask and samples were

periodically removed by syringe to follow the progress of the polymerization by GC.

The runs were terminated after 24 hours when conversion was close to 80%.

5 *Example 4b.* Hybrid catalyst system based on HPPA resin (hydroxypicolylamine)

4b

Composition				
HPPA resin	65 mg		1.44e-4 mol ligand	1.56e-2 mol/L
CuBr	16.5 mg		1.15e-4 mol	1.25e-2 mol/L
CuBr$_2$	7.3 mg		3.31e-5 mol	3.59e-3 mol/L
MMA	4.325 g	4.62 mL	4.32e-2 mol	4.68 mol/L
Toluene		4.62 mL		
2-bromopropionitrile	1.93e-2 g	12.4 μL	1.44e-4 mol	1.56e-2 mol/L
Me$_6$TREN		1.14 μL	4.31e-6 mol	4.67e-4 mol/L

[MMA]:[Initiator]:[HPPA ligand]:[Me$_6$TREN]:[Cu(I)Br]:[Cu(II)Br2] = 300 : 1 : 1: 0.03:

0.80: 0.23.

Tp = 90 °C

10 *Example 5.*   *Use of XVS 43578 as the resin support. (bispicolylamine - CuBr/CuBr2*

(8/2 mol/mol))

5a   [Comparison run]

Composition

XVS 43578 (metallated)	172 mg		1.44e-4 mol Cu	1.56e-2 mol/L
MMA	4.325 g	4.62 mL	4.32e-2 mol	4.68 mol/L
Toluene		4.62 mL		
2-bromopropionitrile	1.93e-2 g	12.4 µL	1.44e-4 mol	1.56e-2 mol/L

[MMA] : [Initiator] : [XVS- Cu(I)Br] : [XVS-Cu(II)Br$_2$] = 300 : 1 : 0.8 : 0.2   Tp = 90 $^\circ$C

5b.   *Hybrid catalyst system based on XVS 43578 resin (bispicolylamine)*

5b

Composition

XVS43578 resin	65 mg		1.44e-4 mol ligand	1.56e-2 mol/L
CuBr	16.5 mg		1.15e-4 mol	1.25e-2 mol/L
CuBr$_2$	7.3 mg		3.31e-5 mol	3.59e-3 mol/L
MMA	4.325 g	4.62 mL	4.32e-2 mol	4.68 mol/L
Toluene		4.62 mL		
2-bromopropionitrile	1.93e-2 g	12.4 µL	1.44e-4 mol	1.56e-2 mol/L
Me$_6$TREN		1.14 µL	4.31e-6 mol	4.67e-4 mol/L

[MMA]:[Initiator]:[XVS ligand]:[Me$_6$TREN]:[Cu(I)Br]:[Cu(II)Br2] = 300 : 1 : 1: 0.03:   0.80:

0.23.   Tp = 90 $^\circ$C

Both control polymerization runs showed linear increase of conversion with time

but no increase of molecular weight with conversion, which suggest very poor

deactivation of growing radical. This can be attributed to the poor accessibility of

growing radical to the Cu(II) centers on support resins even though some 20% of the

transition metal sites are in the form of the redox conjugate. Narrower MWD was seen

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when the soluble ligand was added.

5c.   *Hybrid catalyst system based on XVS 43578 resin (DOW ion exchange*

resin, bispicolylamine) with 3 mol% of Me$_6$TREN-CuBr$_2$ to bispicolylamine .

The XVS 43578 resin was tested for MMA polymerization with 3 mol% soluble

5   Me$_6$TREN/ CuBr$_2$, compared to attached the concentration of the attached

bicpicolylamine-CuBr. The Me$_6$TREN-CuBr$_2$ complex was made in separate stock

solution with acetone prior to use.

Ratio of [MMA] : [2-bromopropionitrile] : [bispicolylamine-CuBr] : [Me$_6$TREN-CuBr$_2$] =

300:1:1:0.03.

10   5c.

Chemical	g	mL	mol	mol/L
XVS 43578	0.124		1.04e-4 ligand	1.56e-2
MMA	3.12	3.34	3.12e-2	4.68
Me$_6$TREN		#	3.12e-6	4.68e-4
CuBr$_2$		#	3.12e-6	4.68e-4
Acetone		1.06		
toluene		2.27		
2-bromopropionitrile	1.39e-2	8.99e-3	1.04e-4	1.56e-2

Reaction condition: temperature, 90 °C; time, 18 h, [MMA]:[2-

bromopropionitrile]:[bispicolylamine-CuBr]:[Me$_6$TREN-CuBr$_2$]= 300:1:1:0.03;

added from stock solution (Stock solution, CuBr$_2$ (3.80e-5 mol)+Me$_6$TREN(3.80e-5

mol) in 13 mL acetone).

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The conversion curve showed very nice linear first order kinetic plot. The molecular weight distribution was still fairly narrow (~1.5) and the molecular weight increased linearly although it was higher that the theoretical line. GPC curves showed very nice shift with conversion suggesting very good control over polymerization.

The polymerization results are summarized below.

Sample	time(h)	Conversion	Mn	Mn(th)	Mw/Mn
1	1.5000	0.19744	18360	5923.0	1.5500
2	3.3300	0.36493	22570	10947	1.5400
3	7.0000	0.49295	31660	15227	1.5100
4	18.000	0.88795	39780	26638	1.4900

Example 6. Polymerization of MMA with bpy-CuBr supported on PS bead(8 μm) (Newly prepared catalyst) – PTH12

Newly prepared catalyst was examined for MMA polymerization without any additional Me6TREN to form a free catalyst in homogeneous phase.

6a. [Comparison Run]

Feedstock				
PS(S)-062600-2	71 mg		7.95e-5 mol	1.56e-2 mol/L
MMA	2.388 g	2.55 mL	2.39e-2 mol	4.69 mol/L
Toluene		2.55 mL		
2-bromopropionitrile		6.87 μL	7.95e-5 mol	1.56e-2 mol/L

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[MMA] : [Initiator] : [PS- Cu(I)Br] : [PS-Cu(II)Br$_2$] = 300 : 1 : 0.8 : 0.2, Tp = 90 °C

The conversion did not increase linearly with time and the molecular weight of the polymer as measured by GPC curves did not change with conversion suggesting that the overall control of polymerization was bad. It seems that the activation is very fast with very slow deactivation because of the poor accessibility of growing radical to Cu(II) centers

6b. Polymerization of MMA with bpy-CuBr supported on PS bead(8 μm) using Me$_6$TREN-CuBr$_2$ – 3% of Me$_6$TREN-CuBr$_2$ to attached bpy.

6b.

Chemical	mg	mL	mol	mol/L
PS bead-bpy-CuBr	126		1.45e-4	1.56e-2
MMA	4.36	4.65	4.35e-2	4.67
toluene		4.65		
2-bromopropionitrile	19.4	12.5e-3	1.45e-4	1.56e-2
Me$_6$TREN	1.00	1.15e-3	4.35e-6	4.67e-4
CuBr$_2$	1		4.35e-6	4.67e-4

Reaction conditions: temperature, 90 °C; time, 24 h,

[MMA]:[2-bromopropionitrile]:[bpy-CuBr r]:[Me$_6$TREN-CuBr$_2$]= 300:1:1:0.03.

The conversion increased continuously and the MWD was very narrow (~1.2). Nice GPC curve shift was observed as the molecular weight increased.

6c. Polymerization of MMA with bpy-CuBr supported on PS bead(8 μm) with

Me₆TREN-CuBr₂ – 1% of Me₆TREN-CuBr₂ to supported bpy.

A polystyrene based ion exchange resin-bpy-CuBr/Me₆TREN-CuBr₂ hybrid

catalyst was tested for MMA polymerization with 1 mol% of Me₆TREN-CuBr₂ to bpy-

CuBr available in the polymerization mixture.   This is part of an effort to determine a

5   lower level for the amount of Me₆TREN-CuBr₂ which is added to control the reaction.

The same recipe and reaction conditions as example 6a were used except only 1% of

Me₆TREN-CuBr₂ was added. [MMA]:[2-bromopropionitrile]:[bpy-CuBr]:[Me₆TREN-

CuBr₂]= 300:1:1:0.01. MWD was around 1.2 and nice GPC shift was observed.

6d.   Polymerization of MMA with bpy-CuBr supported on PS bead(8 µm) using

10   *Me₆TREN ligand only – 1% of Me₆TREN to bpy – without the addition of CuBr₂ –.*

PS bead-bpy-CuBr/ Me₆TREN hybrid catalyst was tested for MMA

polymerization with 1% of Me₆TREN ligand to bpy-CuBr. This is different from previous

experiment (Run No. 6c), since CuBr2 was not added. Only 1% of Me₆TREN ligand was

added to the system. By doing this, it is expected that Me₆TREN can extract sufficient

15   Cu catalyst from the support because the binding constant for Me₆TREN is much higher

than that for bpy.   It is much easier to handle the chemicals because Me₆TREN is liquid

and can be measured by syringe. [MMA]:[2-bromopropionitrile]:[bpy-CuBr

r]:[Me₆TREN]= 300:1:1:0.01.

Run No. 6d.

Chemical	g	mL	mol	mol/L
PS-bpy-CuBr	64e-3		7.36e-5 ligand	1.56e-2
MMA	2.21	2.36	2.21e-2	4.67
Me$_6$TREN	1.746e-4	0.2e-3	7.59e-7	1.60e-4
toluene		2.36		
2-bromopropionitrile		6.36e-3	7.36e-5	1.56e-2

Reaction condition: temperature, 90 °C; time, 34 h, [MMA]:[2-bromopropionitrile]:[bpy-

CuBr]:[Me$_6$TREN]= 300:1:1:0.01

The conversion increased with time and the molecular weight distribution was

still very narrow (~1.2) and showed linear increase of molecular weight, Figure 4. GPC

curves are shown in Figure 5 and display a very nice shift with conversion indicating

very good control over polymerization.

6e.   Polymerization of MMA with bpy-CuBr supported on PS bead(8 μm) with 0.3 mol%

of Me$_6$TREN-CuBr$_2$ to bpy

The PS bead-bpy-CuBr/TREN hybrid catalyst was tested for MMA

polymerization with 0.3 mol% Me$_6$TREN/ CuBr$_2$ to attached bpy-CuBr. Because it is

very difficult to handle this tiny amount of chemicals, first stock solution of Me$_6$TREN-

CuBr2 was prepared using acetone.

[MMA]:[2-bromopropionitrile]:[bpy-CuBr]:[Me$_6$TREN]= 300:1:1:0.003.

6e

Chemical	g	mL	mol	mol/L
PS-bpy-CuBr	72e-3		8.28e-5 ligand	1.56e-2
MMA	2.48	2.65	2.48e-2	4.68
Me$_6$TREN		From stock solution	5.50e-5	4.67e-5
CuBr$_2$		From stock solution	5.5e-5	4.67e-5
Acetone		0.65		
toluene		2.00		
2-bromopropionitrile	11.1e-3	7.2e-3	8.28e-5	1.56e-2

Reaction condition: temperature, 90 °C; time, 24 h, [MMA]:[2-bromopropionitrile]:[bpy-CuBr]:[Me$_6$TREN-CuBr$_2$]= 300:1:1:0.003; Stock solution, CuBr$_2$ (3.80e-6 mol)+Me6TREN(3.80e-6mol) in 10 mL acetone.

5   The conversion curve showed very nice linear first order kinetic plot. The molecular weight distribution was still very narrow (~1.3) and the molecular weight increased linearly although it was higher that the theoretical line. GPC curves showed very nice shift with conversion suggesting very good control over polymerization only with 0.3 mol % of free Me$_6$TREN to attached bpy.

10

Summary Table 1. Methyl Methacrylate and Methyl Acrylate Polymerization with Hybrid Catalysts

Exp No.	Monomer	Hybrid ratio (mol%)	$w_0(Cu)/w_0(monomer)$ (ppm)	Polym. time (h)	Conv. (%)	M_n ($\times 10^3$)	M_n (th.) ($\times 10^3$)	M_w/M_n	$w(Cu)/w(polymer)$ (ppm)
6a immo	MMA	0	0	16	59.0	71.2	17.7	2.26	n.d.[f]
6b	MMA	100	2100	22	61.8	43.7	18.5	1.73	n.d.[f]
6c	MMA	3	63	24	83.0	26.8	25.0	1.19	107
6d	MMA	1	21	17	89.1	32.4	26.7	1.25	27
6e	MMA	0.3	6	24	96.9	35.5	29.0	1.29	15
DP100MMA	MMA	1	21	5.5	91.6	14.3	9.2	1.32	n.d.[f]
Cu0	MMA	1	21	5.5	92.5	40.0	27.7	1.58	n.d.[f]
MA	MA	1	25	51	84.7	21.5	22.6	1.09	n.d.[f]
Sty	sty	1	20	8	51.9	15.0	15.6	1.26	n.d.[f]

[f] Catalyst = $(CuBr/CuBr_2)/Me_6TREN$ (0.97/0.03).

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Example 7. Polymerization of MA with bpy-CuBr supported on PS bead(8 μm) using

Me$_6$TREN-CuBr2 – 1 % of Me$_6$TREN-CuBr2 to bpy-CuBr

PS bead-bpy-CuBr/Me6TREN-CuBr2 hybrid catalyst was tested for MA

5 polymerization with 1 mol% of Me6TREN-CuBr2 to bpy-CuBr. First a stock solution of

Me$_6$TREN-CuBr2 was prepared in acetone.

[MMA]:[2-bromopropionitrile]:[bpy-CuBr]:[Me$_6$TREN-CuBr2]= 300:1:1:0.01.

Run No. 7. [PTH24]

Chemical	G	mL	mol	mol/L
PS-bpy-CuBr	87e-3		1.01e-4 ligand	1.51e-2
MA	2.61	2.73	3.02e-2	5.53
Me$_6$TREN-CiBr2 (from stock sol'n)			1.01e-6	1.51e-4
Acetone		0.35		
toluene		2.38		
2-bromopropionitrile	1.35e-2	8.7e-3	1.01e-4	1.51e-2

Polymerization condition: Monomer = Methyl acrylate

10 [MA]$_0$:[I]$_0$:[bpy-CuBr]$_0$:[Me6TREN-CuBr2]$_0$=300:1:1:0.01, Me6TREN-CuBr2 from stock

solution in acetone.   [MA]$_0$ = 5.55 mol/L; MA/toluene/acetone = 1/0.87/0.13 v/v/v;

temperature = 70 oC. The conversion curve showed very nice linear first order kinetic

plot. The molecular weight distribution was very narrow (~1.1) and the molecular weight

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increased linearly with very good agreement with the theoretical molecular weight. The shape of the GPC curves were very symmetrical and the curves showed clear shift to higher molecular weight region with conversion suggesting very good control over polymerization.

5   The polymerization results are summarized below.

Sample No.	time(h)	Conversion	Mn	Mn(th)	Mw/Mn
PTH24-2	4.5000	0.021669	3832.0	516.00	1.2280
PTH24-3	8.0000	0.089882	5590.0	2321.0	1.2200
PTH24-4	24.000	0.47581	15700	12288	1.1100
PTH24-5	38.000	0.69215	18500	17876	1.1000
PTH24-6	51.000	0.94256	21500	22614	1.0900

Example 8. Polymerization of MMA with bpy-CuBr supported on PS bead(8 μm) using

PMDETA-CuBr2 – 1 % of PMDETA-CuBr2 to bpy-CuBr

15   PS(8 μm)-bpy-CuBr catalyst with 1 mol% of PMDETA was tested for MMA polymerization. This is the repeat of PTH25 to confirm the result.

Experiment PTH50

Chemical	g	mL	mol	mol/L
PS(8 μm)-bpy-CuBr	0.093		6.94e-5	
MMA	2.084	2.23	2.08e-2	
toluene		2.03		
2-bromopropionitrile	9.30e-3	6.00e-3	6.94e-5	
Me$_6$TREN-CuBr2 (from stock			6.94e-7	

sol'n)	
Acetone	0.17
Anisole	0.2

Polymerization condition: Monomer = MMA

[MMA]$_0$:[I]$_0$:[PS-bpy-CuBr]$_0$:[Me$_6$TREN-CuBr2]$_0$=300:1:1:0.01, Me$_6$TREN-CuBr2 from

stock solution in acetone (CuBr2 = 2.38e-5 mol, Me$_6$TREN = 2.38e-5 mol, acetone 10

mL), [MMA]$_0$ = 4.45 mol/L; MMA/solvent (toluene+anisole)= 1/1 (v/v); temperature = 90

oC.

The polymerization results are summarized below.

Sample No.	time(h)	Conversion	Mn	Mn, th	Mw/Mn
PTH50-1	2.0000	0.63678	21450	19106	1.3360
PTH50-2	5.0000	0.76529	28550	22990	1.3520
PTH50-3	16.500	0.89859	32130	26995	1.4730

The molecular weight is much closer to the theoretical value and the MWD

is around 1.3~1.4.

Example 9. Polymerization of MMA with bpy-CuBr supported on PS bead(8 µm) using

dMbpy (dimethyl bpy)-CuBr2 — 1 % of dMbpy-CuBr2 to bpy-CuBr –PTH26

PS bead-bpy-CuBr/dMbpy-CuBr2 hybrid catalyst was tested for MMA

polymerization with 1 mol% of dMbpy-CuBr2 to bpy-CuBr. Stock solution of dMbpy-

CuBr2 was prepared in acetone. However, even in acetone the complex was not fully

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soluble. Regardless of the solubility, a calculated part of the stock solution was added

by syringe. [MMA]:[2-bromopropionitrile]:[bpy-CuBr]:[dMbpy-CuBr2]= 300:1:1:0.01.

Run No. PTH26

Chemical	g	mL	mol	mol/L
PS-bpy-CuBr	86e-3		9.89e-5 ligand	1.66e-2
MMA	2.78	2.97	2.77e-2	4.67
dMbpy-CuBr2 (from stock sol'n)			9.89e-7	1.66e-4
Acetone		0.2		
toluene		2.77		
2-bromopropionitrile	1.33e-2	8.55e-3	9.89e-5	1.66e-2

Polymerization condition: Monomer = Methyl methacrylate

5    $[MMA]_0$:$[I]_0$:$[bpy-CuBr]_0$:$[dMbpy-CuBr2]_0$=300:1:1:0.01, dMbpy-CuBr2 from stock

solution in acetone (not fully soluble) $[MMA]_0$ = 4.67 mol/L; MMA/toluene/acetone =

1/0.92/0.08 v/v/v; temperature = 90 oC.

The conversion curve showed linear first order kinetic plot. However, the

molecular weight distribution was very relatively broad (~1.5) and the molecular weight

10   did not increased linearly.   The shape of the GPC curves were not symmetrical and

the curves did not show any shift to higher molecular weight region with conversion

suggesting poor control over polymerization originating from the lack of shuttling power

of dMbpy (same ligand as the ligand on the support).

The polymerization results are summarized below.

Sample No.	time(h)	Conversion	Mn	Mw/Mn
PTH26-1	2.3000	0.46103	31510	1.4460
PTH26-2	4.0000	0.48036	33630	1.4850
PTH26-4	20.000	0.83297	32160	1.5580

Example 10.   Polymerization of MMA with bpy-CuBr supported on PS bead(8 µm)

using dnNbpy (di-nonyl bpy)-CuBr2 – 1 mol% of dnNbpy-CuBr2 to PS-bpy-CuBr

-

10a.   MMA polymerization was tested with dnNbpy as a soluble deactivator.

The dnNbpy-CuBr2 complex was formed prior to introduction into the reactor.

Run No. PTH27

Chemical	g	mL	mol	mol/L
PS-bpy-CuBr	0.106		1.221e-4	1.557e-2
MMA	3.667	3.92	3.663e-2	4.67
dnNbpy-CuBr2 (from stock sol'n)			1.221e-6	1.557e-4
Acetone		0.2		
toluene		3.72		
2-bromopropionitrile	1.636e-2	10.55e-3	1.221e-4	1.557e-2

Reaction conditions: temperature, 90 °C; time, 17 h, [MMA]:[2-bromopropionitrile]:[bpy-CuBr on PS bead]:[dnNbpy-CuBr2]= 300:1:1:0.01; dnNbpy-CuBr2 stock solution in acetone (CuBr2 = 6.11e-5 mol, dnNbpy = 6.11e-5 mol, acetone 10 mL)

The conversion increase with time and but the first order kinetic plot was not linear. The molecular weight distribution was broad (~1.5) and showed no linear

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increase of molecular weight. GPC curves showed no shift with conversion. These results indicate the control over the polymerization was poor with dnNbpy as a soluble deactivator.

The polymerization results are summarized below.

5

Sample No.	time(h)	Conversion	Mn	Mw/Mn
PTH27-1	1.0000	0.15581	40940	1.9600
PTH27-2	3.0000	0.46864	31100	2.0000
PTH27-3	7.7000	0.77670	36030	1.7980
PTH27-3	17.000	0.89252	35950	1.7350

10b.   *Polymerization of MMA with bpy-CuBr supported on PS bead(8 μm)(Regenerated from PTH 27 experiment) using dnNbpy-CuBr2 as soluble deactivator – 1 mol% of dnNbpy-CuBr2 to PS-bpy-CuBr – PTH33*

10   An attempt was made to regenerate the PS bead-bpy-CuBr collected after the PTH27 experiment using Cu wire in toluene solution. The color of the starting material was light green. The color of the resin changed to a light brown at 8 h. The regenerated supported catalyst was tried for methyl methacrylate polymerization.

Run No. PTH33

Chemical	g	mL	mol	mol/L

PS (8 μm)-bpy-CuBr from PTH27	0.1754		2.017e-4	1.55e-2
MMA	6.059	6.473	6.05-2	4.67
dnNbpy-CuBr2 (from stock sol'n)			2.017e-6	1.55e-4
Acetone		1		
toluene		5		
2-bromopropionitrile	2.702 e-2	17.43 e-3	2.017 e-4	1.55e-2
Anisole		0.5		

Reaction conditions: temperature, 90 °C; time, 45 h, [MMA]:[2-bromopropionitrile]:[bpy-CuBr on PS bead]:[dNbpy-CuBr2]= 300:1:1:0.01; dNbpy-CuBr2 stock solution in acetone (CuBr2 = 2.017e-5 mol, dnNbpy = 2.017e-5 mol, acetone 10 mL)

The activity of the catalyst was only 1/3 of the original activity and conversion reached 60 % after 45 h. The molecular weight distribution was relatively narrow (~1.6) and good agreement with theoretical value. The reason for low activity could be attributed to the insufficient regeneration of the supported catalyst ($Cu^{II} \rightarrow Cu^{I}$) or to the loss of Cu during the original polymerization and/or regeneration step.

The polymerization results are summarized below.

Sample No.	time(h)	Conversion	Mn	Mn,th	Mw/Mn
PTH33-1	1.0000	0.061308			
PTH33-2	3.0000	0.32850			
PTH33-3	6.0000	0.36865			
PTH33-4	20.000	0.54073			
PTH33-5	24.000	0.58901			
PTH33-6	30.000	0.60862	15570	18258	1.6290
PTH33-7	45.000	0.59129	13550	17915	1.6440

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10c. Regenerated PS(8 µm)-bpy-CuBr catalyst Polymerization of MMA with

Me6TREN-CuBr2 as soluble deactivator – 1 mol% of Me6TREN-CuBr2 to PS-bpy-CuBr

– PTH47

Regenerated PS(8 µm)-bpy-CuBr catalyst was tested for MMA polymerization to

5   check its activity.

Experiment PTH47

Chemical	g	mL	mol	mol/L
PS(8 µm)-bpy-CuBr regenerated from PTH44, 45, 46	0.073		4.825e-5	
MMA	1.449	1.55	1.447e-2	
toluene		1.35		
2-bromopropionitrile	6.46e-3	4.17e-3	4.825e-5	
Me6TREN-CuBr2 (from stock sol'n)			4.825e-7	
Acetone		0.2		
Anisole		0.2		

Polymerization condition: Monomer = MMA

$[MMA]_0:[I]_0:[PS-bpy-CuBr]_0:[Me6TREN-CuBr2]_0 = 300:1:1:0.01$, Me6TREN-CuBr2 from

stock solution in acetone (CuBr2 = 2.38e-5 mol, Me6TREN = 2.38e-5 mol, acetone 10

10   mL), $[MMA]_0$ = 4.45 mol/L; MMA/solvent (toluene+anisole)= 1/1 (v/v); temperature = 90

oC.

The conversion was relatively fast (~ 85% in 10 h) and excellent control over the

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polymerization with predetermined molecular weight and narrow molecular weight

distribution (~1.3) was obtained with this regenerated catalyst. The GPC traces show

clean increase in molecular weight with conversion and no tailing can be observed.

5   The polymerization results are summarized below.

Sample No.	time(h)	Conversion	Mn	Mn, th	Mw/Mn
PTH47-1	1.0000	0.39968	11230	11990	1.2900
PTH47-2	2.5000	0.54628	16760	16388	1.2810
PTH47-3	5.0000	0.71367	21400	21410	1.2860
PTH47-4	8.0000	0.81093	25050	24327	1.3090
PTH47-5	20.000	0.90551	31010	27165	1.4130

10d.   Polymerization of MMA with the original catalyst – PTH51

As a comparative experiment, the same polymerization was done with original catalyst

(PTH51)

Experiment PTH51

Chemical	g	mL	mol	mol/L
PS(8 μm)-bpy-CuBr original	0.070		5.1989e-5	
MMA	1.562	1.67	1.560e-2	
toluene		1.47		
2-bromopropionitrile	6.97e-3	4.5e-3	5.1989e-5	
Me6TREN-CuBr2 (from stock sol'n)			5.1989e-7	
Acetone		0.22		
Anisole		0.2		

Polymerization condition: Monomer = MMA

$[MMA]_0:[I]_0:[PS-bpy-CuBr]_0:[Me_6TREN-CuBr_2]_0=300:1:1:0.01$, Me6TREN-CuBr2 from

stock solution in acetone (CuBr2 = 2.38e-5 mol, Me6TREN = 2.38e-5 mol, acetone 10

mL), $[MMA]_0$ = 4.45 mol/L; MMA/solvent (toluene+anisole)= 1/1 (v/v); temperature = 90

5 ℃.

The conversion was compared with that from the regenerated catalyst and the

activity of the regenerated catalyst was almost comparable but slightly lower than that of

the original catalyst (80~90%). The control over the polymerization was better for the

regenerated catalyst.

10 *10e.*   *Ligand and Cu content before and after the regeneration*

Ligand and Cu content analysis for the original catalyst and regenerated catalyst

were performed through elemental analysis(CHN and Cu analysis, independently) to

check the difference between the two catalyst.

	Cu content (mol Cu/g cat)	Ligand content (mol ligand/g cat)
Original Catalyst	7.427e-4	1.310e-3
1st regenerated catalyst	6.609e-4	7.99e-4

10f.   Second recycling of PS(8 µm)-bpy-CuBr catalyst: MMA polymerization – PTH 55

The immobilized catalyst used in recycling experiments were carefully collected

and regenerated again following the same procedure. Therefore this is the second

5   regeneration for this catalyst.   The second regeneration catalyst contains 4.752e-4 mol

Cu/ g cat and 5.460e-4 mol Ligand/g cat. The results are compared with the original and

1st regenerated catalysts.

	Cu content	Ligand content
	(mol Cu/g cat)	(mol ligand/g cat)
Original Catalyst	7.427e-4	1.310e-3
1st regenerated catalyst	6.609e-4	7.99e-4
2nd regenerated catalyst	4.752e-4	5.460e-4

As can be seen from the results, it is clear that both the Cu content and Ligand

15   decrease for every regenerated step. This result suggests that the ligand and Cu are

immobilized in the catalyst particle through chemical bonding (not a physical

absorption). If the Cu and ligand is physically absorbed in the particle, then no further

decrease of the content is expected since the particle experienced extensive washing

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steps in the preparation of the original catalyst and the 1st regeneration steps.   The

reason for the decrease of the Cu and ligand content is believed to come from two

factors that would not apply to a commercial system and therefore do not reduce the

utility of the catalyst system. One is the partial fragmentation of the surface layer of the

5   particle, during the severe handling, where the spatial catalyst concentration is high

(higher than the core part). Secondly, residual chloromethyl groups in the catalyst

particle can initiated the polymerization and the mass of the particle increase for each

polymerization steps.

The catalyst obtained after the 2nd regeneration was tested for MMA

10   polymerization.

Experiment PTH55

Chemical	g	mL	mol	mol/L
PS(8 µm)-bpy-CuBr 2nd regenerated	0.058		2.756e-5	
MMA	0.828	0.884	8.268e-3	
toluene		0.784		
Acetone		0.12		
Me6TREN-CuBr2			2.756e-7	
2-bromopropionitrile	3.69e-3	2.38e-3	2.756e-5	
Anisole		0.1		

Polymerization condition: Monomer = MMA

[MMA]$_0$:[I]$_0$:[PS-bpy-CuBr]$_0$:[Me6TREN-CuBr2]$_0$=300:1:1:0.01, Me6TREN-CuBr2 from

stock solution in acetone (CuBr2 = 2.38e-5 mol, Me6TREN = 2.38e-5 mol, acetone 10

mL), [MMA]$_0$ = 4.4 mol/L; MMA/solvent (toluene+anisole)= 1/1 (v/v); temperature = 90

oC.

5   The polymerization results are summarized below.

Sample No.	time(h)	Conversion	Mn	Mn, th	Mw/Mn
PTH55-1	1.0000	0.19682	4040.0	5904.6	1.3100
PTH55-2	3.5000	0.32559	7900.9	9767.7	1.3400
PTH55-3	5.0000	0.039782	8264.9	11934.6	1.4600
PTH55-4	10.000	0.56707	11783	17012.1	1.4900
PTH55-5	29.000	0.69997	16747	20999.1	1.5800

The control over the polymerization was not bad. There was a linear

increase of molecular weight with relative good agreement with the theoretical value.

The MWD was ~1.4. However, a very slow increase of conversion was observed. The

kinetic plots for the polymerization with original, 1st regenerated and 2nd regenerated

10   catalyst show that the activity of the immobilized catalyst decrease for every

regeneration steps. Probably, the regeneration reaction is not enough, which led to the

accumulation of Cu(II) in the immobilized catalyst. Otherwise, it is also likely that the

chloromethyl group initiated the polymerization of MMA and forms the PMMA polymer

coating around the particle, which hinders the approach of the chemicals to the active

catalyst, reduces the activity, consumes the monomer (lower molecular weight than the

theoretical value) and makes the control worse (MWD ~1.4). This can also results in the

reduction of the content of Cu and ligand per g of catalyst as discussed above.

Example 11.   Polymerization of styrene with bpy-CuBr supported on PS

5   *bead(8 μm) using Me6TREN-CuBr2 as soluble deactivator – 1 mol% of Me6TREN-*

CuBr2 – PTH28

11a.   PS bead-bpy-CuBr/Me6TREN-CuBr2 hybrid catalyst was tested for styrene

polymerization with 1 mol% of Me6TREN-CuBr2 to bpy-CuBr. First a stock solution of

Me_6TREN-CuBr2 was prepared in acetone.

10 [styrene]:[2-bromopropionitrile]:[bpy-CuBr]:[Me_6TREN-CuBr2] = 300:1:1:0.01.

Run No. PTH28

Chemical	g	Ml	mol	mol/L
PS-bpy-CuBr	0.149		1.7135e-4	1.41e-2
styrene	5.35	5.89	5.14e-2	4.23
Me6TREN-CuBr2 (from stock sol'n)			1.7135e-6	1.41e-4
Acetone		0.56		
chlorobenzene		5.69		
2-bromopropionitrile	2.30e-2	14.8e-3	1.7135e-4	1.7135e-2

Polymerization condition: Monomer = styrene

[sty]0:[I]0:[PS-bpy-CuBr]0:[Me6TREN-CuBr2]0=300:1:1:0.01, Me6TREN-CuBr2 from

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stock solution in acetone [sty]$_0$ = 4.23 mol/L; styrene/chlorobenzene/acetone =

1/0.97/0.10 v/v/v; temperature = 120 oC.

The conversion curve showed a curvature but the molecular weight

increased linearly up to 60% of conversion with very good agreement with the

5   theoretical molecular weight. The molecular weight distribution was very narrow (~1.1).

The GPC curves showed very clear shift to higher molecular weight region with

conversion up to 60 % suggesting very good control over polymerization.

The polymerization results are summarized below.

Sample No.	time(h)	Conversion	Mn	Mn(th)	Mw/Mn
PTH28-1	0.50000	0.12538	4041.0	3917.0	1.2940
PTH28-2	2.0000	0.28127	11000	8788.0	1.1970
PTH28-3	4.0000	0.40469	15760	12644	1.1750
PTH28-4	8.0000	0.52732	20580	16476	1.1800
PTH28-5	19.000	0.67652	-	-	-
PTH28-6	26.000	0.71605	-	-	-
PTH28-7	47.000	0.79543	-	-	-

Example 12.   Cu leaching test from PS(8 μm)-bpy-CuBr catalyst– MMA polymerization

10   *experiment and the analysis of residual Cu in the PMMA obtained – PTH49*

As part of the effort to clarify whether leaching of Cu from immobilized catalyst is

significant or not (using a UV-vis test it was concluded that the leaching was negligible),

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the MMA polymerization was attempted using PS(8 µm)-bpy-CuBr immobilized catalyst only.

Experiment PTH49

Chemical	g	mL	mol	mol/L
PS(8 µm)-bpy-CuBr	0.087		6.46e-5	
MMA	1.94	2.07	1.94e-2	
Toluene		1.87		
2-bromopropionitrile	8.67e-3	5.58e-3	6.46e-5	
Anisole		0.2		

Polymerization condition: Monomer = MMA

5    $[MMA]_0:[I]_0:[PS\text{-}bpy\text{-}CuBr]_0 = 300:1:1$, $[MMA]_0 = 4.45$ mol/L; MMA/solvent

(toluene+anisole)= 1/1 (v/v); temperature = 90 ºC.

   The polymer solution obtained in the reaction was diluted with 20 mL of THF and

cast onto a glass plate to allow the the solvents to evaporate, which afforded a

transparent PMMA film. The film was analyzed for residual Cu content.   The residual

10   amount of Cu   was < 1ppm   (Analysis by ICP, from Chemisar Laboratories, Inc.)

This result implies that the amount of leaching of the Cu catalyst during the

polymerization is almost negligible.   Thus, the reduction of Cu and ligand content seen

in the catalyst after attempts at regeneration could be attributed to the gradual catalyst

lost during the extensive washing steps.   The reduction of Cu and ligand also suggest

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that probably the catalyst is not homogeneously distributed in the catalyst particle. It is

possible that the Cu catalyst species are distributed mainly in the surface layer of the

catalyst particle and removed gradually by the peeling of the surface layer of the particle

during the extensive laboratory washing steps because the particle is basically

5   mechanically not so tough.

Example 13.   Cu leaching test from PS(8 µm)-bpy-CuBr catalyst with toluene/MMA

under stirring or without stirring – UV-visible investigation

Because of the slightly higher value of residual Cu content in the final polymer

(15 ppm compared to 6 ppm theoretical value, although this is almost negligible

10   difference), and loss of Cu during the regeneration procedures (11% Cu loss), a

leaching test was performed in toluene/MMA solvent (polymerization medium) to check

whether a simple leaching could be happening in the polymerization step or not.

Experiment 1.

PS(8 µm)-bpy-CuBr catalyst   0.145g   1.0769e-4 mol Cu

15   Degassed MMA (MMA:CuBr = 300:1)3.230g 3.46 mL   3.23e-2 mol

Degassed Tol   3.46 mL

MMA/tol = 1/1 (v/v)

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The slurry of the catalyst supported particles were stored under nitrogen for a

week (no stirring) and a 5.5 mL sample of the clear supernatant solution was transferred

to a schelnk tube under nitrogen. UV-vis was performend under nitrogen.   No distinct

peak was observed. To confirm the result, the solution was vacuum dried and tested

5   again with bis(cyclohexanone)oxaldihydrazone to form a complex with Cu(II) in

alcohol(or water) and give strong blue color. The solution was vacuum dried and

ethanol/water (10/2) and bis(cyclohexanone)oxaldihydrazone was under air. The UV-vis

spectrua were taken for this sample with standard solutions.   While a complex signals

was observed at 190~350 nm due to ligand and colorant

10   (bis(cyclohexanone)oxaldihydrazone). No distinct signal was observed above 400 nm.

Experiment 2.

2.75 mL of MMA and 2.75 mL of toluene were added Into residual catalyst in

experiment 1.   The catalyst solution was stirred for overnight (24h) then the catalyst

was allowed to form a sediment to obtain the clear supernatant solution. The solution

15   was checked with UV-vis.   Still no distinct signal was observed.

From these experiments, it seems that there is no distinct leaching of Cu

occurring during the polymerization.

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Example 14.   PS(8 μm)-bpy-CuBr catalyst particle morphology: Original and after the

regeneration – Optical microscope observation

One question raised in the above discussion is whether the catalyst particle can

retain its original shape during the catalyst preparation and regeneration steps, the

5   catalyst particle morphology of the original one (PS(8 μm)-bpy-CuBr catalyst particle)

and the regenerated one were observed by optical microscope.   The original catalyst

particle (left) exhibited discrete spherical morphology. The size of the catalyst was

approximately 5~10 μm, which agreed well with the reported data (Aldrich, 8 μm, 5%

crosslinked) from the supplier.

10   The regenerated particle also exhibited the same discrete spherical morphology, which

is not so different from the original catalyst particle. This observation means that the 8

μm size PS bead particles endure well the shear stresses that were applied during the

whole washing and regeneration steps. However, it is not obvious from this picture

whether the surface layer of the particle was peeled off accounting for the loss of the

15   catalyst species (Cu and ligand) or not.

Example 15.   MMA polymerization with PS(8 μm)-bpy-CuBr/Me$_6$TREN-CuBr$_2$ hybrid

catalyst: DP = 100

This example was run to check the control over the polymerization behavior when a lower DP was targeted.

Experiment PTH52

Chemical	g	mL	mol	mol/L
PS(8 μm)-bpy-CuBr	0.084		6.24e-5	
MMA	0.625	0.67	6.24e-3	
toluene		0.57		
Acetone		0.26		
Me6TREN-CuBr2			6.24e-7	
2-bromopropionitrile	8.36e-3	5.40e-3	6.24e-5	
Anisole		0.1		

Polymerization condition: Monomer = MMA

5 $[MMA]_0:[I]_0:[PS$-bpy-CuBr$]_0:[Me6TREN$-CuBr2$]_0$=100:1:1:0.01, Me6TREN-CuBr2 from stock solution in acetone (CuBr2 = 2.38e-5 mol, Me6TREN = 2.38e-5 mol, acetone 10 mL), $[MMA]_0$ = 3.9 mol/L; MMA/solvent (toluene+anisole)= 1/1 (v/v); temperature = 90 oC.

The polymerization was much faster than when a DP 300 was targeted (t ~20 h).

10 The polymerization was finished in 6 h (~ 3 times faster than DP 300). The control over the polymerization was still retained.

The polymerization results are summarized below.

Sample No.	time(h)	Conversion	Mn	Mn, th	Mw/Mn
PTH52-1	1.0000	0.62378	6749.2	6245.0	1.3600

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PTH52-2	2.0000	0.78212	9001.7	7830.0	1.3000
PTH52-3	3.0000	0.83362	10693	8346.0	1.2900
PTH52-4	5.5000	0.91621	11999	9173.0	1.3200

Example 16.   Large Bead Supported catalyst/soluble catalyst (Me₆TREN) hybrid

catalyst system

16a.   Preparation of PS(50 µm)-bpy-CuBr catalyst

In certain industrial equipment it could be advantageous to use larger particle beads to assist in the macro-flow of the liquid over the solid.   The catalyst system, CuBr with bpy ligand was therefore immobilized on a commercial polystyrene bead which has a bigger bead size (50 µm).

Reactants:

PS bead-Cl (Aldrich Merrifield resin)	5.023 g	1.0197e-2 mol Cl
DMbpy	7.2430 g	3.9312e-2 mol
(IPr)₂NH	5.51 mL	3.9312e-2 mol
nBuLi	15.72 mL	3.9312e-2 mol
THF	130 mL	

The resin was added to a three neck 250 mL round botton flask which was deoxygenated by charging with N2 follow by vacuum, then 50 mL of dry THF and 7.8 mL of (iPr)2NH were added while the flask was immersed in a dryice/acetone bath.

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15.72 mL of n-BuLi was slowly added to this mixture and the resulting mixture was further stirred at −78 °C for 2 h. A solution of dMbpy pre-dissolved in 80 mL of fresh THF at 60 °C was introduced dropwise and the reaction stirred at -78 °C for an additional 2 h. The reaction temperature was slowly increased to room temperature

5 and stirred for additional 14 h. The resulting product was thoroughly washed two times with toluene, five time THF and with MeOH three times. Drying under vacuum gave yellow powder of the polystyrene bead with attached ligand.

16b. Metallation with CuBr

Reactants:

10 PS bead-bpy   1.5248 g   3.0953e-3 mol bpy ligand on PS

CuBr   0.444 g   3.0953e-3 mol

Dry THF   60 mL

Into 100mL schlenk flask were introduced 1.5248 g of PSbead(50 μm)-bpy and 0.444 g of CuBr followed by evacuation with high vacuum and refilled with dehydrated

15 nitrogen for three times. After 60 mL of THF was added to the flask to suspend it, the temperature was increased to 70 °C. The reaction mixture was stirred at that temperature for 19 h. The obtained product was washed thoroughly with 60 mL of THF for three times and hexane for two times by decantation. The catalyst was dried under

vacuum to obtain black/brown powder and stored under dry nitrogen.

Example 17.   Polymerization of MMA using PS(50 µm)-bispicolylamine-CuBr catalyst

with 1 mol% of Me6TREN-CuBr2 as soluble deactivator – PTH48 (Repeat of PTH29 to

confirm the result)

5   PS(50 µm)-bispicolylamine-CuBr catalyst was tested for MMA polymerization.

This is the repeat of PTH29 to confirm the result.

Experiment PTH48

Chemical	g	mL	mol	mol/L
PS(50 µm)-bispicolylamine-CuBr	0.086		6.415e-5	
MMA	1.927	2.06	1.924e-2	
toluene		1.86		
2-bromopropionitrile	8.59e-3	5.55e-3	6.415e-5	
Me6TREN-CuBr2 (from stock sol'n)			6.415e-7	
Acetone		0.3		
Anisole		0.2		

Polymerization condition: Monomer = MMA

$[MMA]_0:[I]_0:[PS\text{-}bpy\text{-}CuBr]_0:[Me6TREN\text{-}CuBr2]_0=300:1:1:0.01$, Me6TREN-CuBr2 from

10   stock solution in acetone (CuBr2 = 2.38e-5 mol, Me6TREN = 2.38e-5 mol, acetone 10

mL), $[MMA]_0 = 4.45$ mol/L; MMA/solvent (toluene+anisole)= 1/1 (v/v); temperature = 90

oC.

        The polymerization results are summarized below.

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Sample No.	time(h)	Conversion	Mn	Mn, th	Mw/Mn
PTH48-1	2.0000	0.53379	19500	16036	1.4270
PTH48-2	5.0000	0.69236	30400	20799	1.3640
PTH48-3	16.500	0.90568	42770	27208	1.4320

Control over the polymerization was still not as good as when PS (8 µm)-bpy-

CuBr was used as the supported catalyst. The molecular weight was different from the

theoretical value and the MWD ~1.4.   However, the system was controlled.

*Hybrid catalyst systems based on adsorption/desorption of the transition metal complex*

5   *through hydrogen bonding of the ligand to the added solid.*

Example 17.   CN$_6$TREN was chosen as a first exemplary ligand since this ligand would

be strongly adsorbed onto a polar substrate such as a silica particle.

17a.   Preparation of CN$_6$TREN

The reaction scheme for the preparation of the hexa-substituted triamine ligand is

10   shown in scheme 4.
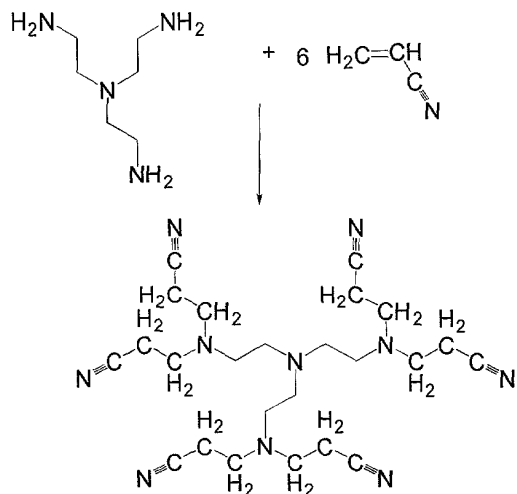
Scheme 4.

Reaction conditions

Chemical	g	mL	mol	mol/L
Tris(2-aminoethyl)amine(TREN)	2.578		1.765e-2	0.654
Acrylonitrile	5.622	6.98	0.106	3.929
Methanol		20		

Reaction temperature and time; 0 °C for 15 min, 40 °C for 3 h, 25 °C for 24 h, 70 °C 68

h, successively.

The conversion was followed by GC analysis and was complete after 64 hr.   At

the end of the reaction period the reaction liquid was subjected to high vacuum to

remove all possible volatile species. A yellow viscous liquid was obtained. To check the

chemical structure of the compound, Mass Spectroscopy and NMR were performed.

CN_6TREN has a MW = 464.25 and a molecular peak at 465.4 (M + H^+) was observed

from mass spectroscopy, which suggest the formation of CN_6TREN.   ^{1}H-NMR

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spectrum was also consistent with the formation of CN$_6$TREN.

17b.   Polymerization of MMA with "free" CN$_6$TREN

Run No. 17b

Chemical	mg	mL	mol	mol/L
CN6TREN	66.9		1.44e-4	1.56e-2
CuBr	20.7		1.44e-4	1.56e-2
MMA		4.62	4.32e-2	4.67
2-bromopropionitrile		12.3e-3	1.44e-4	1.56e-2
Toluene		4.62		

Reaction condition: temperature, 90 °C; time, 16 h, [MMA]:[2-

bromopropionitrile]:[CN$_6$TREN –CuBr]= 300:1:1.

The molecular weight increased with conversion and molecular weight

distribution was narrow; MWD (~1.3), indicating that a transition metal catalyst

complexed with CN$_6$TREN worked well in ATRP of MMA.

17c.   Polymerization of MMA with CN$_6$TREN in the presence of silica

Run No. 17c

Chemical	mg	mL	mol	mol/L
CN6TREN	66.9		1.44e-4	1.56e-2
CuBr	20.7		1.44e-4	1.56e-2
MMA		4.62	4.32e-2	4.67
2-bromopropionitrile		12.3e-3	1.44e-4	1.56e-2
Silica	1.27e3			
Toluene		4.62		

Reaction condition: temperature, 90 °C; time, 16 h, [MMA]:[2-

bromopropionitrile]:[CN$_6$TREN –CuBr]= 300:1:1, silica was dried under vacuum at 130

°C for 6 h prior to use.

Conversion of MMA to PMMA reached 55 % in 16 h. However, the Mw/Mn was

fairly high (1.93).   Therefore in contrast to the previous experiment example (Run No.

17b), a transition metal complex with CN_6TREN as ligand did not work well in the

5   presence of silica (MWD ~2) as in homogeneous solution.   This indicates that the

complex was strongly absorbed onto the silica surface and as with the ligand supported

catalyst the redox conjugate of the transition metal catalyst was not readily accessible to

the growing active polymer chain.

Example 18.   Evaluation of bispicolyl amine ligands with ureido-4-pyrimidinone group.

10   The initial experiments concentrated on the evaluation of bispicolyl amine

ligands with ureido-4-pyrimidinone group in the ATRP of styrene and methyl acrylate.

18a.   Bispicolyl amine (BPOMA) and bispicolyl amine with ureido-4-pyrimidinone

moiety (BPUMA) were tested as a ligand for the atom transfer radical polymerization

(ATRP) of styrene and methyl acrylate and the results are shown in the table below.

15   Table 18. Atom transfer radical polymerization of styrene and methyl acrylate using

"free" BPOMA and BPUMA ligands

Monomer	Ligand	Temp (oC)	Time (h)	Conv (%)	Mn,sec	Mn,th	Mw/Mn
St	BPOMA	110	7.2	59	11580	11800	1.14

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MA	BPOMA	50	14.0	69	16250	13850	1.25
St	BPUMA	110	5.2	57	12700	11400	1.22
MA	BPUMA	50	28.7	52	12220	10400	1.26
MMAa	BPOMA	50	3.1	22	7320	4400	1.45
MMAa	BUPMA	50	5.6	58	16800	11600	1.47

Reaction conditions :

For styrene, [Styrene] = 4.3 M, anisole/styrene = 1/1 (v/v),

[Styrene]:[PEBr]:[CuBr]:[Ligand] = 192:1:1:;

For methyl acrylate, [MA] = 5.6 M, anisole/methyl acrylate = 1/1 (v/v),

5   [MA]:[MBP]:[CuBr]:[Ligand] = 232:1:1:1

BPOMA = N,N-bis(2-pyridylmethyl)octylamine, BPUMA = N,N-bis(2-

pyridylmethyl)octylamine ligand with ureido-4-pyrimidinone moiety

a. [MMA] = 4.6 M, [MMA]/ [EtBriBu] = 200, , anisole/methyl methacrylate

[EtBriBu]/[CuX]/[Ligand] = 2/1/1

10   Good control over the styrene and methyl acrylate polymerization was observed

with both ligands. As shown in the table polymers with low polydispersity (M_w/M_n = ~1.2)

with predictable molecular weight ($M_{n,sec}$ ~ $M_{n,th}$) were obtained at the conversion of

around 60 %.   An examination of the semilogarithmic kinetic plot and the variation of

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molecular weight with conversion in both the styrene and methyl acrylate

polymerizations showed linear semilogarithmic kinetic plot and a linear increases of

molecular weight with a good agreement with the theoretical values, confirming the

good control over the polymerization with BPUMA ligand.   However when compared

5   to BPOMA, the control of polymerization is not quite as good when BPUMA is used.

This can partially attributed to the fact that the complex formed between CuBr and

BUPMA does not completely dissolve in the non-polar /weak polar medium, thus

making the deactivation process is not as efficient as when the CuBr/ BPOMA complex

is used as the catalyst.   Therefore the polymers obtained by using CuBr/BPUMA have

10   boarder molecular weight distributions.   Two approaches were taken to increase the

solubility of the CuX/BUPMA complex.   The first was use of a solvent such as DMF,

(50% v/v with monomer), for the polymerization of methyl acrylate using BUPMA as the

ligand.   The system become a homogenous solution at 50 C, when such a large

amount of solvent is used, and conversion reached 54% conversion after 24 hours;

15   molecular weight 9860, PDI 1.48.

The other approach was to increase the reaction temperature.   The

polymerization was conducted at 70C with the same ratio of reactants and although the

solubility of the complex increased it is still not an homogenous solution.   The

polymerization reach 68% conversion at 3.6 hours, molecular weight 14830, PDI 1.25.

Overall, the BPUMA was confirmed to be a good ligand for ATRP.

Ligand attached to inorganic supports.

Example 19.   Silica supported diamine ligand.

5   *19a.   Synthesis of N,N,N'-trimethyl-N'[3-(trimethoxysilylporpoxycarbonyl)ethyl]-*

ethylenediamine
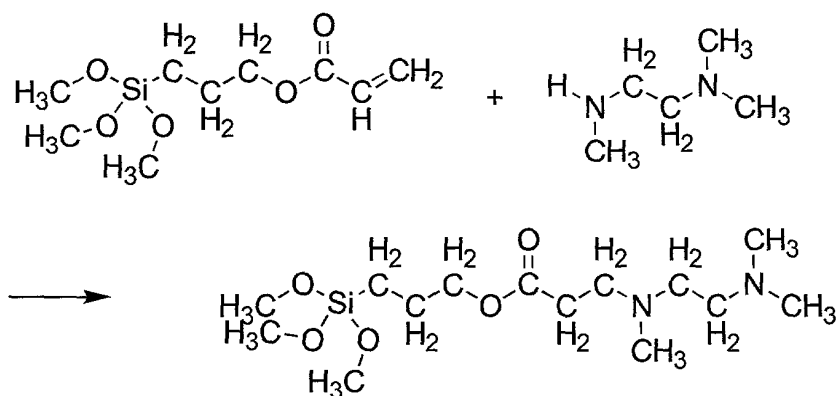
Diamine ligand for ATRP catalyst with trimethoxy silyl group for the

10   immobilization on silica was synthesized through Micheal addition reaction of amine.

Reaction recipe

Chemical	g	mL	mol
3-(triemthoxysilylpropyl)acrylate	10	9.48	4.27e-2
N,N,N'-trimethylethylenediamine	5.24	6.66	5.13e-2
			(1.2 times excess)

Reaction condition: temperature, 25 °C; time, 47 h.

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Procedure: Into a three neck flask equipped with a dropping funnel and

charged with N_2 was added 10 g of 3-(triemthoxysilylpropyl)acrylate at 0°C. N,N,N'-

trimethylethylenediamine was introduced into the reactor dropwise for 1 h. The reaction

mixture was stirred further at 0°C and the temperature was increased to room

5 temperature. The conversion of the reaction was checked by the disappearance of

acrylate peak around 6 ppm in ^{1}H-NMR analysis. The reaction was completed in 47 h.

The high vacuum was applied to the reaction mixture to remove unreacted excess

N,N,N'-trimethylethylenediamine.   The ^{1}H-NMR spectrum of the compound showed.
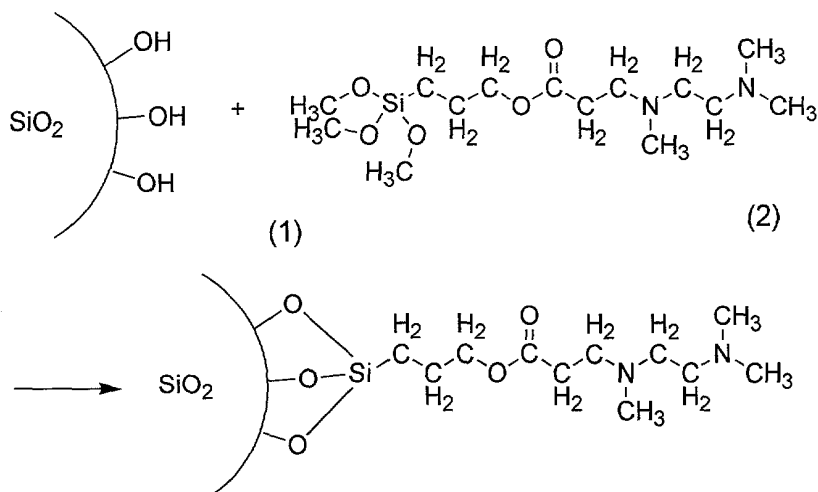
^{1}H-NMR (CDCl$_3$) δ: 3.90 ppm (t, 2H, COOCH_2); 3.40 ppm (s, 9H, SiOCH_3); 2.60 ppm (t,

10 2H, CH_2COO); 2.35 ppm (m, 4H, CH_2N); 2.25 ppm (t, 2H, NCH_2CH$_2$COO); 2.10 ppm (s,

9H, NCH_3); 1.60 ppm (m, 2H, SiCH$_2$CH_2); 0.50 ppm (t, 2H, SiCH_2) which is consistent

with the desired structure.

19b.   Preparation of silica supported trimethyldiamine - CuBr catalyst

15

Scheme 5.

The silica supported trimethylethylene diamine was prepared through the

reaction scheme 5.

Reaction recipe

Chemical	g	mL	mol
Silicaa (1)	3.87		
Diamine ligand (2)	1.95		5.795e-3
Dry THF		30	

5   Reaction condition: temperature, 70 °C; time, 42 h.

a Silica was dried at 135 °C under vacuum for 72 h prior to use.

Procedure: Into a 250 mL three-neck flask charged with N_2 was added 3.87

g of silica under nitrogen. 1.95g of diamine ligand (2)   was weighed separately and add

to the reaction flask with 30 mL of dry THF. The reaction was performed at 70 °C for 42

10   h. After the reaction, a high vacuum was applied to the reaction flask to remove THF

and washed with 40 mL of dry, degassed THF for 4 times through decantation method.

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19c   Preparation of silica supported trimethylethylene diamine-CuBr catalyst –

SDC-112900

The prepared silica supported ligand was metallated with CuBr.

Reaction recipe

Chemical	g	mL	mol
Silica supported diamine ligand	2.322		2.312e-3 (assuming 100% yield in previous rxn)
CuBr	0.3318		2.312e-3
Dry THF		30	

5   Reaction condition: temperature, 60 °C; time, 18 h.

Procedure: Into a 250 mL three-neck flask charged with N_2 was added

2.322 g of silica-supported ligand under nitrogen. 0.3318g of CuBr was weighed

separately and add to the reaction flask followed by the vacuum and N_2 for 3 times.

Degassed, dry THF was introduced to the reaction mixture to suspend the silica and the

10   reaction was performed at 60 °C 18 h. After the reaction, a high vacuum was applied to

the reaction flask to remove THF and washed with 40 mL of dry, degassed THF for 4

times through decantation method. Finally, the reaction product was obtained through

evaporation of THF. A blue powder was obtained.

Example 20.   Polymerization of MMA, MA and styrene with of silica supported

15   *trimethylethylenediamine-CuBr catalyst*

20a. Polymerization of MMA – SDA2

Silica supported trimethylethylenediamine-CuBr catalyst was tested for MMA

polymerization.

Run No. SDA2

Chemical	g	mL	mol	mol/L
SDC-112900	0.2338		1.62e-4	1.56e-2
MMA	4.85	5.18	4.847e-2	4.69
Toluene		5.18		
2-bromopropionitrile	2.16e-2	14.0e-3	1.62e-4	1.56e-2

5   Reaction conditions: temperature, 90 °C; time, 20 h, [MMA]:[2-

bromopropionitrile]:[dimethylethylenetriamine-CuBr on silica] = 300:1:1

GPC curves did not show a clean shift of curves with conversion and indicate

the immobilized catalyst alone can't control the polymerization.

20b. Polymerization of MA – SDA3

10   Silica supported trimethylethylenediamine-CuBr catalyst was tested for MA

polymerization

Run No. SDA3

Chemical	g	mL	mol	mol/L
SDC-112900	0.3183		2.20e-4	1.85e-2
MA	5.68	5.94	6.6e-2	5.6
Toluene		4.94		
Anisole		1		
2-bromopropionitrile	2.95e-2	19.0e-3	2.20e-4	1.85e-2

Reaction conditions: temperature, 70 °C; time, 50 h, [MA]:[2-

bromopropionitrile]:[dimethylethylenetriamine-CuBr on silica] = 300:1:1

The first order kinetic plot exhibited linear increase of conversion. However, the

molecular weight distribution was broad (~2.0) and showed no increase in the molecular

weight. GPC curves showed no shift with conversion and indicate the immobilized

catalyst alone can't control the polymerization of MA.

20c.   Polymerization of styrene – SDA4

Silica supported trimethylethylenediamine-CuBr catalyst was tested for styrene

polymerization

Run No. SDA4

Chemical	g	mL	mol	mol/L
SDC-112900	0.361		2.49e-4	1.45e-2
Styrene	7.79	8.57	7.48e-2	4.36
Chlorobenzene		7.57		
Anisole		1		
PEBr	4.6e-2	34.0e-3	2.49e-4	1.45e-

Reaction conditions: temperature, 110 °C; time, 25 h,

[styrene]:[PEBr]:[dimethylethylenetriamine-CuBr on silica] = 300:1:1

The first order kinetic plot exhibited linear increase of conversion. However, the

molecular weight distribution was broad (>2.0) and showed no increase in the molecular

weight. GPC curves are shown below and showed no distinct shift with conversion.and

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indicate the immobilized catalyst alone can't control the polymerization.

20d.   Polymerization of MMA with silica supported trimethylethylenediamine-CuBr

catalyst using Me6TREN-CuBr2 as soluble deactivator – 1 mol% of Me6TREN-CuBr2 –

PTH30

5   Silica supported trimethylethylenediamine-CuBr catalyst was tested for MMA

polymerization with 1 mol% of Me6TREN-CuBr2 as a soluble deactivator to

trimethylethylenediamine-CuBr. Please compare this result with DA2 experiment in this

monthly report. You will find a clear improvement on the control over the polymerization

with hybrid catalyst system.

10   Run No. PTH30

Chemical	g	mL	mol	mol/L
SDC-112900	0.2366		1.635e-4	1.563e-2
MMA	4.91	5.25	4.905e-2	4.69
Me6TREN-CuBr2 (from stock sol'n)			1.635e-6	1.563e-4
Acetone		0.55		
Toluene		4.71		
2-bromopropionitrile	2.19e-2	14.1e-3	1.635e-4	1.563e-2

Reaction conditions: temperature, 90 °C; time, 20 h, [MMA]:[2 bromopropionitrile] :

[dimethylethylenetriamine-CuBr on silica] : [Me6TREN-CuBr2] = 300:1:1:0.01;

Me6TREN-CuBr2 stock solution in acetone (CuBr2 = 4.5e-5 mol, Me6TREN = 4.5e-5

mol, acetone 15 mL

The first order kinetic plot exhibited linear increase of conversion. The molecular

weight distribution was narrow (~1.3) and showed linear increase of molecular weight.

The number average molecular weight was almost identical with the theoretical one.

GPC curves show a clean shift with conversion.

5   These results indicate the hybrid catalyst system is applicable to the other

immobilized system such as trimethylethylenediamine which is supported on silica.

The polymerization results are summarized below.

Sample No.	time(h)	Conversion	Mn	Mw/Mn
PTH30-1	1.0000	0.16899	11250	1.8120
PTH30-2	3.0000	0.65799	24110	1.3150
PTH30-3	5.0000	0.80539	32820	1.2700
PTH30-4	9.0000	0.93385	37000	1.2900
PTH30-5	20.000	0.96643	-	-